Application of commercial Xylanases in Bleaching - A Review

Mathur Shobhit, Kumar S. and Rao N.J.

ABSTRACT

Bleaching of kraft pulp using a combination of chlorination & alkaline extraction has been practiced for many years. Unfortunately the bleach plant effluents contains high chlororganics which are bioaccumulating, have high AOX, color, BOD & COD loads. Today the pulp & paper industry is under growing pressures from authorities, consumers & environmental groups to reduce the effluent loads by using clean bleaching technologies that reduce or eliminate the chlorine/chlorine based chemicals use. Alternative bleaching methods using oxygen & ozone peroxide etc. have been developed but are quite expensive to adopt & hence are only viable to large paper mills. Enzyme prebleaching is considered as one viable alternative.

The most important enzyme known to enhance bleaching is xylanase. Many commercial xylanases are available from a variety of suppliers. These biotechnological processes are highly specific in action, require milder conditions and generate less pollution loads as compared to chemical processes.

The biobleaching process with xylanase has been commercialised in Scandanavia, North America, Japan, Czeckoslovakia & Denmark. Many mill trials have also been conducted in Sweden, Canada and Finland. A mill trial using commercial xylanase B230 from BIL Australia has been done on bagasse and wood pulp giving encouraging results. The commercial enzyme in combination with conventional and TCF bleaching sequences have given encouraging results in terms of reduced bleach chemical demand, increased brightness ceiling and improved paper properties. Reduction in chlorine usage in part due to xylanase treatment has shown to substantially lower the level of AOX generation.

The biotechnology applications at prebleaching stage appears economically viable. It is time that Indian mills start looking at biobleaching as a option to not only improve the mill performance environmentally but to reduce input costs. The current status in the field is reviewd.

INTRODUCTION

The bleaching of pulp is done to remove lignin and to increase the brightness. Bleaching of kraft pulp using a combination of chlorination & alkaline extraction has been practiced for many years. Unfortunately the bleach plant effluents contains high chlororganics making the effluent toxic & bioaccumulating. These effluents also have high AOX, color, BOD & COD loads. Today the pulp & paper industry is under growing pressures from authorities,

Institute of Paper Technology
P.O. Box No. 83,
Saharanpur - 247 001 (U.P.)

consumers & environmental groups to reduce the effluent loads from the mills. The issue is to develop clean bleaching technologies that reduce or eliminate the chlorine/chlorine based chemicals in pulp bleaching. To reduce chlorine & chlorine compounds in bleaching which are the most polluting, industries/ researchers have developed alternative bleaching methods which use oxygen & ozone, peroxide etc., but these are quite expensive to adopt, since they require lot of changes in the infrastructure & hence are only viable to large paper mills. Enzyme prebleaching is considered as a viable alternative. The biotechnological processes are highly specific in nature, require milder conditions and generate less pollution as compared to chemical processes. Xylanase are the most popular enzymes used in prebleaching.

USE OF XYLANASE ENZYME

Hemicellulases especially Xylanases have been used for prebleaching of pulps. The use of Xylanase enzyme for bleaching of kraft pulp was introduced by Viikari etal in 1986 (1) and was further developed using enzyme extracts from a number of microbial sources (2-5). It was understood that enzymatic pretreatment could not enable the production of fully bleached pulp but could increase the final brightness ceiling and help to reduce the consumption of chlorine based chemicals in bleaching. Later the enzymatic treatment was combined with more efficient pulping and non chlorine bleaching methods. Combination of enzymatic treatment with different bleaching sequences gives the most reliable and practical results. The main enzyme used for enzymatic pretreatment of kraft pulps is reported to be B-Xylanase.

PRODUCTION OF HEMICELLULASES/ XYLANASES

Fungal xylanases of Aspergillus and Trichoderma species as well as bacterial xylanases from Bacillus, Streptomyces and Clostridium species have been extensively studied (10). The strains reported to be used for commercial production of xylanases include T.reesei, T. lanuginosus, Aureobasidium pullulans and Streptomyces livindans. (6-9) Various commercial xylanases have been manufactured by a number of companies as shown in Table -1.

The efficiency of various commercial xylanases for pretreatment of softwood and hardwood pulps before bleaching has been evaluated and many of them have reached pilot stage or full commercial stage.

Table-1

Reference as given in book "Enzymes in pulp and paper industries"

Product	Supplier
Irgazyme 40-4X/	Generator, Finland/
Albazyme 40-4X	Ciba Geigy, Switzerland
Irazyme-10A/	Generator, Finland
Albazyme 10A	Ciba Geigy, Switzerland
Bleachzyme F	Biocon India, Bangalore
Bleachzyme E	Biocon India, Bangalore
B-230	Esvin Bio Systems, India
Cartazyme HS	Clariant, U.K.
Cartazyme HT	Clariant, U.K.
Cartazyme SR 10	Clariant, U.K.
Ecopulp X-100	Primalco Biotech, Finland
Ecopulp X-200	Alco Ltd., Biotechnology, Finland
Ecopulp X-200/4	Alco ICI, Finland
Ecopulp TX-100	Primalco Biotech, Finland
Ecopulp TX-200	Primalco Biotech, Finland
Ecopulp XM	Primalco Biortech, Finland
Ecozyme	Zeneca Bioproducts/ICI, Canada
GS-35	Iogen Corporation, Canada
HS-70	Iogen Corporation, Canada
Hemicellulose	Amano pharmaceutical
Amano 90	Co., Japan
Ingrazyme 40s	Genecor, Finland
Novozyme 473	Novo Nordisk, Denmark
Optipulp L-800	Solvay Interox, USA
Pulpzyme HA	Novo Nordisk, Denmark
Pulpzyme HB	Novo Nordisk, Denmark
Pulpzyme HC	Novo Nordisk, Denmark
VAI Xylanase	Voest Alpine, Austria

Xylanase pretreatment was shown to be more effective with hardwood than softwood (10). Enzyme pretreatment was also subjected to bamboo, wheatstraw and bagasse pulps (11-13). Xylanase pretreatment

Table-2

Effect of xylanase Treatment on Conventional Bleaching for Various Kappa Factor and Chlorine Dioxide Sustitutions of Hardwood Pulps (14)

Bleaching sequence C/D EDED

Chlorine Dioxide Substitution (%)	Control		Treated	
	Kappa Factor	Final Brightness (% ISO)	Kappa Factor	Final Brightness (%ISO)
10	0.200	90.00	0.05	90.0
	0.233	90.2	0.10	90.8
	0.266	90.3	0.15	91.8
40	0.15	89.2	0.05	90.0
	0.173	90.0	0.10	90.8
	0.200	91.0	0.15	91.8
70	0.200	90.0	0.05	88.7
	0.233	90.6	0.10	90.0
	0.250	90.9	0.15	90.3
100	0.150	83.5	0.10	87.4
	0.173	85.3	0.15	87.4
	0.200	87.0		

Bleaching sequence : C/DEDED.

Table-3

Total Chlorine and Chlorine Dioxide charges needed to achieve 90% ISO brightness for xylanase-pretreated and untreated Hardwood Pulps (15).

Chlorine Dioxide Substitution (%)	Total Chlorine Charge on Pulp (%) Control	Treated
10	6.75	4.55
40	6.25	4.70
70	7.00	5.05

either improved brightness or reduced chlorine, Chlorine dioxide and peroxide requirement and had no adverse effect on pulp viscosity or mechanical properties.

EFFECT OF XYLANASES PRETREATMENT ON PULP BLEACHING

This has been discussed in the following:

Table-3A

Biobleaching Trials with B230

Mill No.	Raw Material	Pulp Type	Present Bleach Sequence	Proposed Bleach Sequence	Target Brightness (ISO)	Lab Status	Scale Brightness Achieved (%)	Reduction In Perioxide (%)	Pilot Status	Scale Brightness Achieved (%)	Reduction In Perioxide %)
1.	Bagasse	Chemical Pulp	C-E/H-H	X-P-H-H	+80	Completed	83.2	50	In progress	78-79	50
2.	Wood	Dissolving Grade	C-E-H	X-P-H-H	+90	Completed	91-92	50			
3.	Wood	CMP	P	X-P	68-70 (PV)	Completed	70(PV)	25	In progress		
4.	Wood	CSRMP	P	X-P	60	In progress	58	28	In progress		
5.	Wood	Dissolving Grade	C-Eo-H-D	X-P-H-D	+90	In progress	90	20	In progress		
6.	Bagasse	Mechanical Pulp	P	X-P	50	In progress	50	30	In progress		

Table-4

Effect of Xylanase Treatment on Brightness of Eucalyptus Kraft Pulp in CEH/CEHH Bleaching Sequence (24)
Kappa no. of unbleached pulp 25.5

Enzyme	Bleaching Sequence	Brightness (% ISO) Control	Enzyme	Increase in Brightness Due to Enzyme Treatment (Points)
Cartazyme HS-10	CEHH	80.4	84.2	3.8
	CEH	78.1	83.0	4.9
Novozyme 473	CEHH	80.6	83.6	3.0
VAI xylanase	CEHH	80.4	82.5	2.1

Based on data from Ref. 24

Kappa number of unbleached pulp : 25.5

a) Factors affecting treatment efficiency

b) Effect on bleach chemical requirements and brightness

c) Effect on pulp properties/strength

d) Effect on bleach effluents

FACTORS AFFECTING TREATMENT EFFICIENCY

The optimum operating conditions for enzyme pretreatment with respect to pH, enzyme dosage, reaction time are needed to be established for a given pulp - enzyme system however the following values are reported to be giving good results.

Table-5

Effect of Xylanase Treatment on bleach chemical consumption in bamboo pulp bleaching (21).

Bleaching sequence	**Enzyme**	**Bleaching chemicals, kg/metric ton pulp**				**Reduction in bleaching chemicals due to enzyme, kg/metric ton pulp**			
		Cl_2	**NaOH**	**Hypo**	**ClO_2**	**Cl_2**	**NaOH**	**Hypo**	**ClO_2**
C_DEHD	-	47.0	30.0	35.4	8.5	-	-	-	-
XC_DEHD	0.20	37.6	29.1	35.4	8.5	9.4	0.9	-	-
XC_DEHD	0.20	47.0	29.1	35.4	4.5	-	0.9	-	4.0
XC_DEHD	0.20	47.0	28.6	30.0	6.5	-	1.4	5.4	2.0

Kappa no. of Pulp = 23.3

Enzyme Bleachzyme E

Kappa No. of Pulp 23.3

Bleach Sequence (Cd)EHD

Brightness Traget 87% ISO

TABLE- 6 Analysis of softwood pulp effluents following xylanase treatment (28).

Sequence	**Chlorine multiple**	**C-stage residual % on pulp**	**(C+D)EpDED Brightness % ISO**	**BOD mg/L**	**COD mg/L**	**BOD/ COD**	**TOC ppm**	**Toxicity,* %solution**	**AOX ppm**
Control									
W(C+D)Ep	0.15	-	88.1	51	600	0.085	503	33.2	42.7
W(C+D)Ep	0.22	0.04	92.8	50	800	0.063	668	24.3	65.1
Xylanase-treated									
X(C+D)Ep	0.10	-	85.8	102	75.6	0.14	585	53.9	22.7
X(C+D)Ep	0.15	-	91.6	113	948	0.12	787	25.6	43.5
X(C+D)Ep	0.18	0.32	94.1	120	926	0.13	752	22.7	68.4
W (control stage)				<50	58	0.86	54	100	-
X(xylanase stage)				78	370	0.21	291	100	-

Substitution of ClO_2 in chlorination stage: 20%.

Kappa no. of control pulp: 28.3; kappa no. of xylanase-treated pulp: 26.3. Residual less than 0.001% on pulp.

Note: Effluent determinations made on combined W or X(C+D)Ep stage.

TABLE-7

Analysis of hardwood pulp E1-stage effluents* following xylanase treatment (28).

Sequence	Chlorine multiple	(DC)EDED Brightness % ISO	BOD mg/L	COD mg/L	BOD/ COD	TOC ppm	Toxicity, % solution	AOX ppm
Control								
W(DC)E	0.15	89.3	261	1100	0.24	429	8.9	17.6
W(DC)E	0.20	90.3	259	1160	0.22	464	8.8	25.3
Xylanase-treated								
X(DC)E	0.10	89.5	212	956	0.22	385	4.9	13.3
X(C+D)Ep	0.10	89.1	283	906	0.31	379	6.6	7.5
X(C+D)Ep	0.10	89.3	280	988	0.28	402	4.8	7.5

Substitution of ClO_2 in chlorination stage: 20%.

Kappa no. of control pulp: 12.2; of xylanase-treated pulp: 11.6.

Note: Effluent determinations made on combined W or X(C+D)Ep stage.

TABLE-8

Optimum reaction conditions for various commercial enzymets.

Enzyme	pH	Temp. °C	ENZYME DOSE kg/metric ton pulp	ENZYME DOSE IU/g pulp	Reaction time, h
Pulpzyme HA_x	5-5.5	40-45	0.5	5	3
Cartazyme HS-10	4-5	40-55	0.2	13	3
VAI xylanase	5-7	50-60	0.7	3.5	3
Irgazyme-10	5.5-6	40-50	0.8	12	3
Bleachzyme B	7-7.5	40-50	1.0	10	3
Bleachzyme F	6-6.5	45-50	0.2	6	3
Hemicellulose Amano-90*	4.5-5	45-50	0.2	15	3
Ecopulp X-200	5-6	50-55	0.5	10	3
Bleachzyme*	4-5	34-40	5.0	5.5	3
Pulpzyme HB	7-8	50-60	0.5	7.5	3
Pulpzyme HC	8-9	60-70	1.0	14	3

Cellulase side activity present.

(a) Enzyme pH

Fungal orign - 4-6

Bacterial orign - 6-9

(b) Dosage (IU/gm pulp) - 2-5

(c) Pulp consistency - to give uniform dispersion

(d) Reaction time - 2 hrs.

Pulp washing after enzyme treatment is not necessary (30).

Bajpai et al in 1996 compared pretreatment of a number of commercial xylanases on Bamboo kraft pulp. The pH, temperature, enzyme dose and reaction time were evaluated. As it can be seen from the Table 8 different types of enzyme have different optimal conditions for treatment (25).

EFFECT ON BLEACH CHEMICAL REQUIREMENTS AND BRIGHTNESS

The reduction in Cl_2 for various levels of substitution by ClO_2 for softwood and hardwood pulps using various commercial enzymes have been studied (15-26). Table 2 and 3 show show the effectiveness of xylanase in bleaching hardwood and softwood pulps in bleaching hardwood and softwood pulps in bleaching sequence (CD) EDED. Reduction in active Cl_2 consumption between 16-25% has been reported using alkaline xylanase at different levels of ClO_2 substitution with improvement in targeted brightness levels.

The effect of enzyme on oxygen pretreatea pulps has been studied for hardwood and softwood pulp (18-19). Similar enzyme pretreatment was done on wheat straw pulp leading to improved bleach results. Some eco pulps have been made using xylanase (21-23) chlorine free bleaching sequences.

Bajpai et.al studied the effect of commercial xylanase pretreatment on brightness of Eucalyptus kraft pulp in conventional bleaching sequence (CEHH & CEH) There was increase in brightness for all enzymes as shown in Table 4 (24). They also showed reduction in bleach chemicals by pretreating bamboo pulp with Bleachzyme E produced by Biocon, India in CDEHD bleaching sequence as shown in Table 5 (25). An Australian based microbial enzyme B230 was evaluated in collaboration with Esvin Biosystems, Madras. The enzyme pretreatment increased the brightness and consumption of bleach chemicals by 25% in bleaching of chemical bagasse pulp (C-E/H-H bleaching sequence). Likewise in case of mechanical grade of pulp the enzyme treatment resulted in significant reduction in consumption of hydrogen peroxide in bleaching. There was no perceptible change in strength & optical properties when the microbial enzyme was used (26) as shown in table 3A.

EFFECT ON PULP PROPERTIES/ STRENGTH

The enzyme - treated pulps show unchanged or improved strength properties (24). Improved viscosity also been reported. However, the viscosity of the pulp was adversely affected when cellulase activity was present (26).

EFFECT ON BLEACH EFFLUENTS

Xylanase pretreatment has led to reduced effluent concentration of AOX and dioxin as less chlorine is needed to achieve a given brightness. The AOX concentration in the combined effluent after and E1 stage were reduced. The effluent BOD almost doubled and there was increase in chemical oxygen demand (COD) & total organic carbon (TOC). The BOD/ COD ratio also increased indicating the effluent was more amendable to biological degradation in a secondary treatment plant. Effluent toxicity remained essentially the same. In the same study, xylanase pretreatment of a hardwood kraft pulp under the same conditions led to a reduction of 35-40% in chlorination charge. E, stage AOX was 24% less than in the control and the BOD/COD ratio was increased. Also the organochlorine content of the pulp was reduced by 41% at a chlorine dioxide substitution level of 40% as shown in table 6 & 7, (28). Bajpai et al reported that the TOCL content in extraction stage effluent was reduced by 30% when the pulp was first pretreated with xylanase and then subjected to CEH bleaching (29). Similar results were reported for effluents on bamboo pulp using Pulpzyme E (25).

XYLANASE TREATMENT & MILL TRIALS

Recently xylanase pretreatment has attained the commercial status. Several mill scale trials have also been conducted. Presently a significant number of Scandanavian and North American mills are bleaching entirly with xylanases (31-34). The biobleaching process with xylanase has also been commercialised in Japan, Czeckoslovakia & Denmark.

TABLE-9

Biobleaching Process-Saving in Peroxide-Cost Benefit to the Mill

Mill	Raw Material	Pulp Type	Capacity tpd	Present Bleach Sequence	Proposed Bleach Sequence	Peroxide Dosage % Actual	After Erzyme Treatment	Saving in Peroxide TPD	kgs/tonne of pulp	Saving Rs. per tonne of pulp
1.	Bagasse	CMP	150	P	X-P	3.00	1.95	1.58	10.50	204.00
2.	Wood	CTMP	60	P	X-P	4.50	3.37	0.68	11.30	226.00
3.	Wood	CSRMP	200	P-H	X-P-H	3.50	2.45	2.10	10.50	210.00
4.	Wood	Dissolving Grade	200	C-Eo-H-E-D	X-P-H-D	4.00	3.00	2.00	10.00	200.00
5.	Bagasse	Semi Chemical	50	C-E-H	X-P-H-H	2.50	1.25	0.63	2.60	250.00
6.	Wood	CMP	200	P	X-P	5.00	3.50	3.00	15.00	300.00

Xylanases have been used to obtain the following benefits, depending upon the needs of the various mills:

- decrease AOX discharges, primarily by decreasing chlorine gas usage
- eliminate chlorine gas usage for mills at high chlorine dioxide substitution levels
- eliminate bottlenecks in mills limited by chlorine dioxide generator capacity
- increase the brightness ceiling, particularly for mills contemplating ECF and TCF bleaching sequences
- decrease bleaching costs, particularly for mills using large amounts of peroxide or chlorine dioxide.

In areas of ECF and TCF biobleaching, xylanases trials have been conducted by 50% of Candian pulp and paper mills by 1996 and six ECF mills are using xylanase regularly (35). Stricter Canadian environmental regulations have resulted in the use of xylanase in bleach plants more than any other country (36).

Xylanase prebleaching can be used to reduce active chlorine consumption and AOX emissions or to increase brightness. Results of mill trials on prebleaching of kraft pulp with the enzyme preparation Irgazyme 40 show a 20 and 15% reduction in the consumption of active chlorine and alkali, respectively (37).

Metra- sellu Bkp mill in Aanekoski was arguably the first large scale trials to take place anywhere in the world. In these tests, which were conducted on pine (Pinus) and birch (Betula) softwood and hardwood pulps, the pulp was subjected to a Albazyme-10 enzyme treatment at pH 4-7 at 50-70°C with a retention time of 1-3 hr. Softwood pulps showed the greatest potential for bleaching chemical reduction, with a 20% reduction in chlorine consumption & 15% in active chlorine in the first bleaching stage. All 35,000 to of enzyme-pretreated pulp produced during the 4-week trial was used within the Metsa Serla group for fine-paper, board, and wood-containing printing grades (38).

The addition of the xylanase enzyme Albazyme 10 to the screened, acidified brownstock (at pH 5.5) before HD storage reduced chlorine dioxide consumption by 15% and produced a comparable reduction in bleach-plant effluent AOX. Pulp strength, cleanliness, and birghtness properties were unchanged (39) in the trials conducted at Canadian Forest Products Mill in Prince George producing softwood BKP using D (E_{OP}) DED bleach sequence.

The use of xylanase to cleave the covalent linkages that were formed between xylan and residual lignin during kraft pulping makes lignin removal easier during bleaching so that either brighter pulps can be produced for the same amount of bleaching agent or a lower chlorine multiple can be used. A successful trial at Canfor Corp.s Intercontinental mill in British Columbia, Canada, is reported, in which the use of xylanase reduced chlorine dioxide consumption by 16%. New xylanase have been produced with activities that are optimum at pH and temperature ranges close to those of the kraft process, and xylanases with optimum activities at pH 10-11 and 90°C, resp., are being developed (40).

Albazyme-10 and other commercial xylanases have been used in 3 different mills to-

(i) overcome ClO_2 capacity limitation to increase ECF pulp production, to increase brightness, to reduce AOX levels and reduce chlorine consumption (41-45).

Bajpai etal have reported that many Finnish companies-Enso Gutseit OY, Kimi Kymmene, Metsa-Sellu OY, Sunila OY, Vetisiluoto OY and United Paper Mills-are conducting research to develop chlorine-free bleaching which involves the use of enzymes, oxygen, peroxide and ozone.

ECONOMICS OF XYLANASE PRE-TREATMENT

Enzymes have been used not only to overcome capacity limitation in ECF bleaching sequences but also to reduce bleaching costs and improve pulp quality (46).

Bajpai et al have reported that a saving of U.S. $ 10,000 to US. $ 100,000 by using enzymes. In 1995, the approximate cost of enzyme was around U.S. $2 per metric ton of pulp. The prices of enzymes have decreased due to advances in production strains and technologies. Due to the low enzyme price and low capital costs of the enzyme stage, the potential economic benefits of enzyme bleaching are significant. A simple calculation of potential relative economic benefits in a ECF sequence reveals that the reduction of approximately 5 kg chlorine dioxide per ton of pulp assuming a chlorine dioxide cost of U.S. $0.70 per kg) leads to a savings of about U.S. $ 5.0 per ton of pulp in chlorine dioxide costs alone. Additional saving in alkali is also expected. The costs of oxygen-based chemical, e.g. hydrogen peroxide and ozone, are even higher, and so the corresponding savings would be even more pronounced. Usually, the cost of enzyme is only slightly less than that of the competing bleaching chemicals based only on price. However, other factors (such as decreased AOX, and retention of viscosity or other technical pulp properties) may lead to additional advantages that are difficult to specify in terms of direct cost. In the future all available technologies will compete with respect to effectiveness as well as price.

Biochemical bleaching research underway at Gist-brocades (Netherlands) indicates saving in bleach plant chemicals of $15/t which amounts to total saving of $500,00 - $10,000,000/yr (47).

Esvin Bio-systems limited showed relevant & economically attractive technology of reducing peroxide consumption in mechanical grade pulps of bagasse & wood by enzyme B230. Taking the cost of peroxide as Rs 20,000/- per ton (50% conc.). They showed a saving of Rs 204/- to Rs 300/- per tonne of paper for various types of pulps as shown in Table 9 (26).

BENEFITS OF ENZYME TREATMENT

The benefits of using enzymes are dependent on the bleaching sequences the pulp. Enzyme pretreatment has been reported to result in higher final brightness or a lower bleaching chemical consumption. Less chlorine/chlorine based chemicals are used to achieve the target brightness. As a result, the AOX load of the bleaching effluent has been reduced. In ECF bleaching sequences, the use of enzymes increases the productivity of the bleaching plant, when the production capacity of chlorine dioxide is a limiting factor. This is often the case when the utilization of chlorine gas has been abandoned. In totally chlorine-free bleaching sequences, the addition of enzymes increases the final brightness value which is a key parameter in marketing of the chlorine-free pulps. In addition to this, the saving in TCF bleaching chemicals is important with respect both costs and strength properties of the pulp. The treatment of karft pulp with cellulase-free xylanases increases pulp viscosity due to partial hydrolysis of low DP xylan in the pulp. In the production of TCF pulps, the use of enzymes enables the preservation of acceptable strength properties.

CONCLUSIONS

The literature review indicates enzyme preblaching (biobleaching) a viable technoeconomic option. However before mills plan application of enzymes some laboratory/pilot plant studies are essential with commercial enzymes to determine optimum:

- Enzyme dosage
- Operating conditions as temperature, pH, and time

- Benefits in terms of environmental improvements
- Economic advantages.

The literature indicates very little information on use of enzymes for non woods particularly straws, this needs a little more detailed study. It is time that Indian mills start looking at biobleaching as a option to not only improve the mill performance environmentally but to reduce input costs.

LEGENDS

C: Chlorination

D: Chlorine dioxide

H: Hypochlorite

E: Extaction

Z: Ozone

X: Enzyme

BOD: Biochemical oxygen demand

COD: Chemical oxygen demand

TOC: Total organic carbon

AOX: Adsorbable organic halogen

TCF: Total Chlorine free

ECF: Elemental Chlorine free.

REFERENCES

1. Viikari, L., Ranua, M., Kantelinen, A., Sundguist, J., Linko, M. (1986) Bleaching with Ezymes. The Third International Conference on Biotechnology in the pulp and paper Industry, Stockholm, 16-19.6.1986, p67-69.

2. Yang, J.L., Lou, G., and Eriksson, K.L., (1992) Tappi J. 75 (12) : 95.

3. Viikari, L., (1990), Biotechnical methods in pulp bleaching, oral presentation at Challenges and possibilities for Biotechnology in the pulp and paper industry, October 17-18, 1990, Hanaholmen, Helsingfors, Finland.

4. Kantelinen, A., Ratto, M., Sundquist, J., Ranua, M., Viikari, L., Linko, M. (1988) Hemicellulases and their potential Role in Bleaching Proceedings. International pulp Bleaching Conference, Orlando, June 5-6, p 1-9.

5. Jurasek, L., Paice, M.G. (1988) Biological Bleaching of pulp, Proceedings. International pulp Bleaching conference, Orlando, June 5-9, p 11-13.

6. Biely, P. Trends Biotechnol., 2 286-290 (1985).

7. Hamilton, J.K., Partlow, E.V. and Thompson, N.S. Tappi J., 41 (12), 803-811 (1958).

8. Senior, D.J. Hamilton, J. and Bernier Jr., R.L. In: Xylans and Xylanases (Visser. J., Beldmann, G., Dusters-Van Soeren, M.A. & Voragen, A.G.J., Eds.) Progress in Biotechnology, Vol. 7, Elsevier, Amstrerdam, pp. 555-558, (1992).

9. Suominen, P., Mantyla, A., Saarelainen, R., Paloheimo, M., Fagerstrom, P., Parkkinen, E. and Nevalainen, H., In: Proc. of the 5th Int. Conf. On Biotechnology in the Pulp and Paper Industry, Kyoto, Japn, May 27-30, pp. 435-439 (1992).

10. Fiserova, M.; Opalena, M.; Vyskummy Ustay Papera a Celulozy. (Bratislava: Slovakia). Use of Xylanases in Kraft Pulp Bleaching. Vyskummy Ustav Papera a Cellulozy (Pulp and Paper Research Institute, VUPC Bulletin, no. 30(3) (Bratislava): 16p. (1994) [Engl.].

11. Bajpai, P., Bajpai, P.K., Tappi, Journal, Vol. 79 no. 4, 1996 p. 225-230.

12. Popa, V.I.; Institution Politehnic. (Jassy: Romania); Spiridon, I.; Study of Enzymatic Treatment's Influence in Obtaining Pulp from Wheat Straw. 8th International Symposium on Wood and Pulping Chemistry, June 6-9 1995, Helsinki, Finland: Proceedings. (2). Poster Presentations (EuCePa, TAPPI, KCL, Japan TAPPI, and (Appita): 461-466 (1995); Gummerus Kirjapaino Oy.) [Engl.).

13. Sivaswamy, S.N., Udayachandran, R., and Venkataraman T.S., Enzymatic Pretreatment of Pulp For Reduction In Consumption of Bleach Chemicals, IPPTa Vol. 10, No. June 1998, p.1-9.

14. Senior, D.J., Hamilton, J., Bernier, R.L., Et al., Tappi J. 75 (11) : 125 (1992).

15. Senior, D.J., and Hamilton, J., Tappi J. 76 (8) : 200 (1993).

16. Hoffmann, G.C., Paper Age (October 1991), p. 26.

17. Munk Niels Enzyme Process Division, Novo Nordisk, Bleach Boosting of Eucalyptus Kraft Pulp (Bioindustrial Group).

18. Pedersen Saaby, Elm. Dana D. Novo Nordisk Bioind. Inc. Aoril, Paper Presented at the 'International Pulp Bleaching Conference' In Stockholm, Sweden, Jue 11-14, 1991.

19. Allison, W., Clark, Thomas and Wrathall, Stephen, Pretreatment of radiata pine kraft pulp with a thermophilic enzyme. Effect of oxygen, ozone and chlorine dioxide bleaching, Appita Vol. 46 No. 5, p-349-353, Oct. 1993.

20. Popa, V.I.; Institution Politechnic. (Jassy : Romania); Spiridon, I.; Study of Enzymatic Treatment's Influence in Obtaining Pulp from Wheat Straw. 8th International Symposium on Wood and Pulping Chemistry, June 609, 1995, Helsinki, Finland: Proceedings. (2). Poster Presentations (EuCePa, TAPPI, KCL, Japan TAPPI, and (Appita) : 461-466 (1995); Gummerus Kirjapaino Oy.) [Engl.].

21. Surma-Slusarska, B.; Leks-Stepien, J.; Comparison of the Action of Different Xylanase Preparations in Bleaching of Kraft Pulps with Oxidative Regeants). Przegl. Paier. 53, no. 8:489-491 (August 1997) [Pol.]

22. Durain, N:, Universidade Estadual de Campinas; Milagres, A.; Biotechnology Centre, Xylanase Delignification in Traditional and Chlorine-Free Bleaching Sequences in Hardwood Kraft Pulps Enzymatic Degradation of Insoluble Carbohydrates (ACS) : 332-338 (1995; ACS). [Engl.].

23. Vicuna, R.; Universidad Catolica. (Santiago : Chile); Oyarzun, E.; Osses, M; Bleaching of Radiata Pine [Pinus radiata] Kraft Pulps with Different Enzymes. 1994 Biological Sciences Symposium; Proceedings (TAPPI) : 253-258 (October 6, 1994; TAPPI Press). [Engl.].

24. Bajpai, P., Bhardwaj, N.K., Bajpai, P.K. and Jauhari, M.B.J. Biotechnol., 36 (1), 1-6 (1994).

25. Bajpai, Pratima and Bajpai, Pramod K., Application of xylanases in prebleaching of bamboo kraft pulp, Tappi Journal, vol. 79, no. 4, p-225-230, April 1996.

26. Srivaswamy, S.N., Udayachandran, R., and Venkataraman, T.S., Enzymatic Pretreatment of Pulp for Reduction in Consumption of Bleach Chemicals, IPPTA vol. 10, No. 2, p-1-8, June 1998.

27. Puls, J., Poutanen, K., and Lin, J.J., Biotechnology in Pulp and Paper Manufacture (T.K. Kirk and H.M. Chang, Eds.), Chap. 16, Butterworth-Heinemann, Raleigh, NC, p. p183 (1990).

28. Senior, D.J. and Hamilton, J., J. Pulp Paper Sci. 18 (5) : J165 (1992).

29. Bajpai, P., Bhardwaj, N.K., Maheshwari, S. and Bajpai, P.K. Appita, 46 (4), 274-276 (1993).

30. Vegega, A.M., Strunk, W.G., Elm, D.D., et al. TAPPI 1993 Pulping Conference Proceedings, Book 3 TAPPI PRESS, Atlanta, p. 1049.

31. Capps. C. World Pap., 220 (7), 42-43 (1995).

32. Lavielle, P. Asia Pacific Papermarker, 3 (5), 29-31 (1993).

33. Lavielle., P. In: Proc. of Pan-Pacific Pulp and Paper Technology; Tokyo, Japan, September 8-10, Part A, pp. 59-64 (1992).

34. Senior, D.J. and Hamilton, J. Pulp and Paper 66 (9), 111-114 (1992).

35. Webb, L; Envirocell. Bio-Opportunities Emerge After Pulping Experiences, Pulp Pap. Eur. 1, n0. 8: 12-15 (October 1996). [Engl.].

36. Senior, D.; Bernhardt, S.; Hamilton, J.; ICI Forest Products; Lundell, R.; Primalco. Mill Implementation of Enzymes in Pulp Manufacture. 1997 Biological Sciences Symposium: Proceedings (TAPPI) : 163-168 (October 19, 1997; TAPPI Press). [Engl.].

37. Freiermuth, B.; Ciba-Geigy AG. (Basel :

Switzerland); Koljonen, M.; Genecor International. (Porkkala-Kantvik : Finland); Werthemann, D.P.; Ciba-Geigy AG. (Basel : Switzerland). Enzymatic Prebleaching of Kraft Pulp: Innovative Technology to Decrease the Demand for Bleaching Chemicals and Reducing AOX Discharges. Progress '93: Needs and Possibilities of Paper Industry Development in the Countries Changing Their Economic System [s]. New Technologies and Equipment for Pulp Manufacturing : 218225 (1993); Stowarzyszenie Papier-Nikow Polskich. [Engl.].

38. Koponen. R.; Metsa-serla Oy. (Aanekoski: Finland) Enzyme Systems Prove Their Potential. Pulp Pap. Int. 33, no. 11: 20, 25 (Nov. 1991). [Engl.].

39. Scott. B.P.; Canadian Forest Products Ltd. (Prince George: B.C. : Canada); Young, f.; Paice, M.G.; Paprican. (Pointe Claire: Qc: Canada). Mill-Scale Enzyme Treatment of a Softwood Kraft Pulp Prior to Bleaching. CPPA Annu. Mtg. (Montreal) Preprints Vol. 79B: 167-173 (Jan. 26-29, 1993). [Engl.].

40. Lavielle, P.; Genencor International. (Paris : France). Xylanase Prebleaching. Asia Pacific Papermaker 3, no. 5: 29-31 (aug. 1993). [Engl.].

41. Lavielle, P.; Koljonen, M.; Genencor International (Redhill: England: U.K.; Piiroinen, P.; Cultor Oy. (Finland) : Koponen, R.; Metsa-Sellu. (Finland); Reid D.; CFI. (UK); Fredriksson, R. Munksjo AB. (Aspa Bruk: Sweden). Three Large Scale Uses of xylanases in Kraft Pulp Bleaching. Proc. Fur. Pulp Pap. Week 4th Int. Conf. New Avail. Tech. Current Trends (Bolognal), Vol. 1 Pulp Pap. Maint : 203-215 (May 19-22, 1992). [Engl.].

42. Scott. B.P.; Candian Forest Products Ltd. (Prince George : British Columbia: Canada); Young, F.; Paice, M.G.; Paperican. (Pointe Claire: Quebec: Canada). Enzyme Pretreatment of Unbleached Softwood Pulp Effectively Reduces Active Chlorine Multiple and AOX Generation. Preprints of Papers to be Presented at the 1992 Spring Conference : Canadian Pulp & Paper Association, Technical Section, Pacific Cost and Western Branches (CPPA), Session 2A:Biobleaching, Paper no. 1:11p. (May 16, 1992; CPPA). [Engl.].

43. Turner, James C., Skerker, Paul S., Burns, Barbara J., Howard, John C., Alonso, Miguel A. and Andres Jose Luis, Bleaching with enzymes instead of chlorine - mill trial, Tappi Journal, p-83-389, December 1992.

44. Trotter 1990, Tappi J. 73:198-204.

45. Sinner M., Kapplmuller K., Schwarzl K. 1992 VAI Report on Mills Scale Trial.

46. Tolan J.; Thibault, L.; Logen. Decreasing ECF-BleachingCosts with Enzymes in a Mill with Oxygen Delignification. Pulp Pap. Can. 98, no. 12: 147-150 (December 1997). [Engl.; Fr. sum.].

47. Lidby, PO, O, Papeterie, (Paris France) no. 187, 34-35, March 1995.