Enzymatic Prebleaching of Kraft Pulps : An Option for Cleaner Production Technology in Indian Paper Industry

Jain R.K., Thakur V. Vasanta, Manthan M., Mathur R.M. & Kulkarni A.G.

ABSTRACT

Changes in public policies, customer preference for environmentally benign products & new market demand have increased the interest in developing bleaching technologies with low AOX levels in the recipient. In response to these demands, various technologies are currently studied and being adopted to reduce or eliminate the use of chlorine and chlorine based chemicals during bleaching. However the application of enzymatic prebleaching has proved to be an up-coming option before the paper industry which has received considerable attention during the recent years.

The use of hemicellulolytic enzymes particularly the xylan attacking enzyme-Xylanases as prebleaching agents are now available and currently in use in commercial bleaching sequence for production of bleached pulp from soft wood and certain species of hardwoods in the developed countries, wherein it has been possible to reduce chlorine demand to a level of 15-20% during bleaching with corresponding reduction in AOX level (20%) and improved pulp brightness to a level of 2-3%ISO.

Central Pulp & Paper Research Institute (CPPRI), as part of its programme on promotion of clean & green technologies in Indian Paper Industry could identify enzymatic prebleaching (Biobleaching) as one of the promising up-coming cleaner production technology option. Extensive studies have been carried out at the institute wherein various xylanase enzymes preparation, both indigenous and the imported commercialy available enzymes have been evaluated on pulps both from wood and non wood based pulp & paper mills employing eucalyptus and bagasse as major fibrous raw materials. Since the effectiveness of a particular xylanase enzyme may vary in respect of its activity purity particularly in terms of cellulase freeness, enzyme pretreatment conditions and the type of pulps, therefore evaluation studies are required to be carried out in order to assess its response on the pulps being produced in paper industry and to develop tailor made enzymes for enzymatic prebleaching of pulp.

The present paper highlights evaluation of various xylanases for their response on chemical pulps in respect of potential of savings of elemental Cl_2 during conventional CEH bleaching stage with gain in pulp brightness and reduction in toxic (AOX) level in bleach effluent, in order to access the potential of promotion of the technology in Indian Paper making. The results have been found to be encouraging.

INTRODUCTION

In the last few years there has been growing pressure for change in the way that chemical pulps are bleached. The traditional & effective approach of using chlorine as a bleaching agent is in less use for environmental concern since the process produces dioxin and other chlorinated organic compounds which

**Central Pulp & Paper Research Institute,
P.O. Box.-174,
Saharanpur-247001 (U.P.)**

contribute to the discharge of AOX. (Adsorbable Organic halides) in the recipient streams. Gaseous chlorine (Cl_2) in particular, but also other chlorine containing bleaching chemicals such as chlorine dioxide (ClO_2) and hypochlorites are blamed for the formation of chlorinated compounds.

Conventional bleaching of Kraft pulp has evolved over the years but there has been particular pressure for change to bleaching sequence like ECF & TCF in Europe & Scandinavian countries. A similar situation also exist in Asian countries particularly in India wherein the pulp & paper mills started switching over to partial ECF bleaching.

Regardless of the pace of change, a market has been created for ECF and TCF pulps and alternatives have to be found to chlorine containing bleaching chemicals or new technologies have to be considered.

The options open to pulp mills considering a change to chlorine free bleaching are substitution of chlorine dioxide, Oxygen delignification & Extended delignification to reduce Kappa No. before bleaching, substitution of hydrogen peroxide and ozone to replace chlorine based chemicals. However, all the process suffers with disadvantages like:

- High capital cost
- Risk of loss in pulp viscosity and strength
- And high cost of bleaching chemicals

This climate of change has provided an opportunity for enzymes as pre-bleaching agents with an basic aim of :-

- Reduction in use of chlorine & chlorinated bleach chemicals
- Reduction in discharge of AOX in bleach effluents.
- Gain in final pulp brightness & improved pulp properties

The enzymes used commercially in pulp bleaching are hemicellulases, which selectively affect the accessible hemicellulose fraction of the pulps. Among various available hemicellulases, xylanases have been found to be more effective as pre-bleaching agents. (1) Xylanase producers are found both among bacteria & fungi. Several criteria are essential for choosing micro -organisms to produce xylanases. In addition to give the desired biobleaching effect, the enzyme must be produced in sufficiently huge quantity & should be completely free of cellulase activity. Any cellulase activity will have serious economic implication in terms of cellulose loss, degraded pulp quality & increased effluent treatment cost (2). Now xylanolytic preparations could be produced by recombinant DNA technology, selective inactivation or bulk scale precipitation. High productivity could be achieved by exhaustive screening, genetic engineering & growth optimisation programmes.

MATERIAL & METHODS

Pulp samples: - Commercial unbleached pulp samples of eucalyptus kraft pulps was procured from large integrated pulp & paper mills & soda bagasse pulp was procured from small agro based paper mills. The pulp then obtained was characterised for its kappa number.

Table-1

List of the enzymes used in the enzymatic prebleaching studies

Xylanase enzyme	Source
Enzyme-1	Imported
Enzyme-2	Indigenous

ENZYME PROCUREMENT

Various xylanase preparation from identified enzyme manufacturing companies were procured. Among which the enzymes are used in the present study in given in Table-1.

ENZYME PRETREATMENT OF PULPS

Xylanase pretreatment of pulp was carried out on 500gm (OD weight) samples in batches. The pulp was adjusted to the required pH by addition of 1 M H_2SO_4 solution where ever required (Table-2) Enzymes were added to the pulp after sufficient dilution & mixed properly by kneading mechanism. Temperature was maintained at 50°C for 2 hours. Pulp consistency was made to 10%. Control pulps were prepared identically to the enzyme treated pulp with enzyme being replaced with water. Table-2 shows the conditions for enzyme treatment of pulp.

Table-2

Enzyme pre-treatment conditions

Enzyme	pH	Temperature °C	Enzyme dose kg/tp/IU/gm	Retention Time (hrs)
Enzyme-1	8.5	50-55	10	2
Enzyme-2	8.5	50	10	2

Enzyme pretreated pulps were subjected to conventional bleaching sequence CEH without washing.

ANALYSIS OF ENZYME TREATED & CONTROL PULP EXTRACTS FOR LIGNIN SUGARS & COLOUR

The extractability of the lignin & chromophores in enzyme pretreated pulp filtrates were analysed by UV measuring the absorbance at 280 nm & 465 nm respectively where as the reducing sugars were estimated by DNS method.

ACTIVITY OF ENZYMES

All the enzyme preparations were tested for filter paper or for cellulose contamination by method of Mandals & Weber (1959) where as xylanase activity was measured by reducing sugar procedure (4).

RESULTS & DISCUSSION

Various sets of experiments on xylanase prebleaching of pulps have been conducted employing Eucalyptus kraft pulp (Eucalyptus + Bamboo) and Bagasse procured from the mills followed by bleaching of pulps using conventional CEH bleaching sequence.

ENZYMATIC PRE-TREATMENT OF WOOD KRAFT PULPS:

EFFECT OF XYLANASE PRE-TREATMENT ON KAPPA NUMBER

From the results in Table-3, it is clearly indicated that there is reduction in kappa number of the unbleached kraft wood pulp after xylanase enzyme pretreatment which could be reduced to about 1.5 points i.e. from initial kappa no. of 17.7 it was reduced to 16.3 and 16.5 respectively with two xylanase preparations. However measurement of kappa no. of the enzyme treated and control pulp can not be taken as reliable indicator of the Klason lignin content since it does not taken in to account the structural difference in the lignin after enzyme treatment (5). Further there was gain in brightness of the unbleached pulp 0.5 to 1.0% ISO point which was improved from 27.5 to 28.0 % & 28.4 % ISO indicating the effectivity of the xylanase enzyme.

EFFECT OF XYLANASE TREATMENT ON BLEACING CHEMICAL REQUIREMENT

xylanase treated pulps differ in response to bleach chemical than untreated pulps (6). Bleaching of the control and enzyme treated pulps using conventional

Results of enzymatic pretreatment of wood pulp (eucalyptus+bamboo) using commercial xylanases

Table-3

Characterization of unbleached pulp before & after enzyme treatment.

Particulars	Control Pulp	Enzyme-1 treated	Enzyme-2 treated
Kappa No. of Pulp	17.7	16.3	16.5
Brightness, % ISO	27.5	28.4	28.0
CED Viscosity, cm^3/g	557	550	604

Table-4a

Bleaching of Pulp using Conventional CEH Sequence Before & After Enzyme Treatment.

Particulars	Control Pulp	Enzyme-1 Treated Pulp	Enzyme-2 Treated Pulp
Chlorination Stage			
% Chlorine Applied	4.2	3.6	3.6
% Chlorine Consumed	98.8	88.4	88.4
Saving in Chlorine, %	---	14	14
Alkali Extraction Stage			
NaOH, %	1.5	1.5	1.5
%, NaOH Consumed	57.7	46.6	58.3
Final pH	11.53	11.66	11.21
Kappa No.	4.3	3.2	3.3
Hypo Stage			
%, Applied	2.0	2.0	2.0
%, Consumed	94	88	83
Final Brightness of the pulp, % ISO	80.6	83.8	83.7
Brightness gain, %	--	3.2	3.1

Table-4b Strength & Optical Properties of Wood Pulp (Eucalyptus+Bamboo) Before & After Enzyme Treatment.

Particulars	Control Pulp	Enzyme-1 Treated Pulp	Enzyme-2 Treated Pulp
Strength Properties			
Revolution, PFI	4000	4000	4000
Freeness, CSF	160	185	215
Apparent density, g/m^3	0.82	0.84	0.79
Burst Index, kPam^2/g	4.10	3.80	4.10
Tensile Index, N.m/g	64.0	60.5	64.0
Tear Index mNm^2/g	5.50	4.9	4.9
Optical Properties			
Brightness, % ISO	65.7	68.0	68.7
Opacity, %	92.2	91.2	91.2

Table-5

Characteristics of bleach effluent (CEH stage) of enzyme pretreated & untreated eucalyptus kraft pulp.

Particulars	Untreated pulp	Enzyme-1 Treated effluent	Enzyme-2 Treated effluent
COD kg/tp	19.57	25.87	31.92
BOD kg/tp	3.42	7.11	9.06
AOX kg/tp	2.12	1.80	1.80

CEH bleach sequence showed remarkable reduction in the requirement of chemical chlorine which was reduced from 4.2% (42.00 kg/tp) to 3.6% (36.00 kg/tp) in case of both enzyme treated pulps. Following the alkali extraction & hypo stage its brightness gain in bleached pulp could be achieved to a level of 3.0 % ISO points i.e. the final brightness was improved from 80.6% ISO to 83.7% ISO respectively with both xylanase enzymes (Table - 4a). Xylanase treatment has remarkable effect on the yield of the pulp as possible explanation for the effect of xylanase treatment as reduction in the requirement of the chlorine might be that xylanase effects the removal of specificlignin structures, leaving a residual lignin in the pulp which may be more responsive to bleach chemical oxidation than the residual lignin in conventional pulps (7,8). Thus the quantities of the lignin represented by kappa factor of around 0.2 in conventional and enzyme treated pulp might not be identical but actually, lower in the enzyme treated pulp. More over the lignin in the enzyme treated pulp may respond better to oxidative bleach chemicals. The enzyme treated pulp samples which contains comparatively lower lignin are bleached to a higher brightness than conventional bleached pulp.

EFFECT OF XYLANASE TREATMENT ON STRENGTH & OPTICAL PROPERTIES OF THE PULP

Extensive studies on evaluation of the xylanases treated pulps with both enzyme preparation indicate that such pulp required equivalent or sometimes more amount of refining energy to refine the pulps to same freeness level than control pulps (8). Determination of the strength properties of both enzyme treated pulps, showed that burst tensile index could be maintained at par which were found to be 3.80 & 4.10 kPa. m^2/g against 4.10 and 60.5 and 64.0 N.m/g against 64.0 of control pulp respectively. Little drop in burst and tensile index in case of enzyme-1 treated pulp could be resulted by reducing the treatment time and/or little enzyme dose. The tear factor was found to almost at par i.e. 4.9 mN.m^2/g in both enzyme treated pulps as against 5.05 in case of control (Table 4b).

Results of CED viscosity determination indicated that the average pulp viscosity was not significantly altered as indicated from the results shown in Table -3.

ENVIRONMENTAL EFFECT OF ENZYME TREATMENT

Reduction in chlorine demand of around 15% during CEH bleach sequence resulted in lowering the toxicity of the bleach plant effluent in enzyme treated pulp which could be reduced to the tune of around 20% as AOX level was reduced from 2.12 kg/tp to 1.8 kg/tp. Results are shown in the Table -5.

XYLANASE PRETREATMENT OF NON WOOD PULPS (BAGASSE)

Results of studies conducted on xylanase pretreatment of non wood pulps (soda bagasse pulp) procured from an agro based mill using xylanase preparation are shown in Table-6.

EFFECT OF XYLANAE PRETREATMENT ON KAPPA NUMBER

There was slight and / or no reduction in kappa number of the pulp after pretreatment and unbleached pulp brightness was improved to 0.5 point. Effect of enzyme pretreatment on bleach chemical requirement & strength & optical properties of the pulp:

Table-6

Enzymatic Prebleaching of soda bagasse Pulp using Xylanase

Table6a Bleaching of Pulp using Conventional CEH Sequence Before & After Enzyme Treatment		
Particulars	**Control**	**Enzyme Treated**
Kappa No.	26.8	26.0
Brightness, % ISO	33.5	34.0
Chlorination		
% Chlorine Applied	5.4	5.4
% Chlorine Consumed	93.3	92.8
Alkali Extraction		
% Alkali Applied	2.0	2.0
% Alkali Consumed	81.4	80.9
Final pH	10.0	10.0
Kappa No.	4.7	4.0
Hypo Stage		
%, Hypo Applied	2.5	2.5
%, Hypo Consumed	91.0	7.9.5
Brightness % ISO	82.0	83.1
Brightness Gained, %	—	1.1

Table-6b Strength Properties of Bagasse Pulp Before & After Enzyme Treatment.		
Particulars	**Control**	**Enzyme Treated**
Revolution, PFI	500	500
Freeness, CSF	290	275
Apparent density, gm/cm^3	0.84	0.85
Burst Index, $kPam^2/g$	3.20	3.50
Tensile Index, N.m/g	55.00	57.0
Tear Index $mN.m^2/g$	4.35	4.40
Fold Kohler Molin (log)	1.41	1.61
Porosity, Bentsen ml/min	26.0	25.0
Optical Properties		
Opacity	76.0	74.80
Yellowness, %	24.5	20.64
Whiteness, %	57.0	58.10

Bleaching carried out using conventional bleach sequence involving CEH with optimised doses of elemental Cl_2 5.4%, alkali extraction & hypo showed improved pulp brightness which was improved from 82% ISO to 83.1% ISO indicating gain of 1.1% ISO (Table-6a).

In one earlier experiment yield losses up to 5% could be reported which on optimisation of the xylanase enzyme doses & time period could be reduced to 2-3% loss in the yield of enzyme treated pulp. It has been observed that too much applied doses of xylanases at longer time period can lead to a decreased pulp yield because of degradation of the hemicellulases. This can further result in less of strength properties too.

Results of the strength & optical properties of bagasse pulp are shown in Table -6b. From the results it is shown that there is an improvement in Burst index, Tensile & Tear index which were increased from 3.20-3.50 kPa.m², 55.0 to 57.0 N.m/g & 4.35 to 4.40 mN.m²/g respectively. The fold kohler was also improved from 1.41 to 1.61 with regards to opical properties of the enzyme treatment pulp besides improved brightness (1.1% ISO). There was an alteration in yellowness & whiteness values i.e. yellowness was reduced from 24.5 to 20.64 with improvement in whiteness from 57.0 to 58.1%.

CONCLUSION

1. Pre-treatment of chemical pulps with xylanase enzymes could improve the bleachability of the pulps in subsequent bleaching stages.
2. Enzyme pre-treatment conditions & the enzyme preparations play significant role in achieving desired targets in terms of reduction in doses of elemental chlorine, pulp brightness gain & maintaining strength properties.
3. It has been possible to reduce the doses of elemental chlorine to the extent of 15% while gaining pulp brightness of 2-3% ISO.
4. Wood Kraft pulps have been found to have better enzyme response than non wood pulps.
5. The technology is highly promising for paper Industry and mills have significant impact on reducing the toxicity of bleach plant effluents when the mills are facing formidable problem of discharge standards particularly the AOX levels.

LITERATURE CITED:

1. Suurnakki, A. Hemicellulases in the bleaching and characterization of kraft pulps. VTT Publications. 267; Technical research centre of Finland; ESPoo, 1996.
2. Dancault, C., and Valade, J.L., Tappi J. 77 (6) : 39 (1992).
3. Farell, R.L., Skerer, P.S. Xylans and xylanases, (J. Visser, Ed.) Elsevier, Amsterdam, 1992.
4. Bailey, M.J., Biely, P and Poutanen, K. Interlaboratory testing methods for assay of xylanase activity, J. Biotechnol. 23:257 (1992).
5. Viikari, L., Ranua, M., Kantelinen, A., Sundquist, J. and Linko, M., Application of enzymes in bleaching, 3rd Intt. conf. Biotechnology pulp and paper Ind., Stockholm, 67-69 (1986)
6. Yiiner, S. and Enstrom, B., Svensk papper. stidn. 60 (15):549 (1992).
7. Clayton, D.W. and stone, J.E., Pulp paper mag. Can. 64 (11) : 459 (1963).
8. Luers, M., Biobleaching at skeena cellulose, 1993 Tappi pulping conference proceedings, Tappi press, Atlanta, p.12.