

Enzyme Pre-Bleaching Towards ECF Pulp: A Successful Attempt at Century Pulp and Paper

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ABSTRACT

With the focus shifting towards Cleaner Production options in terms reduction of Chlorine in the Bleaching Process and subsequently minimal AOX levels in effluent discharges, Century Pulp and Paper conducted detailed studies on Enzyme Prebleaching to ascertain it's effectiveness. The positive results led to successful adoption of 'Bio Bleaching' for different durations in all the three fibre lines the company operates, particularly in Bagasse based pulping where "Elemental Chlorine Free" pulp could be produced with excellent results.

An Alkaline hemicellulase (Xylanase) enzyme was put to optimum use as a Bleach Boosting agent. Enzyme selectively removes xylan from the surface and the pores of the fibres, which facilitates the subsequent bleaching, reducing the bleaching chemicals required to reach the same degree of delignification.

The paper outlines the findings of the pilot and plant scale trials conducted with the enzyme and benefits derived in terms of Enhanced brightness of pulp with lower bleaching chemicals and reduction in AOX levels in the discharged effluents.

INTRODUCTION

Mounting environmental pressure and awareness has led the Paper Industry to look for Cleaner Production options in terms of reduced consumption of chlorine and it's compounds in the bleaching sequences thereby minimising the discharge of chlorinated organics in the effluent i.e. A.O.X. Century Pulp and Paper, adopting a pro-active approach, experimented with enzyme prebleaching for its three fibre lines with an objective to reduce the lignin content entering the bleach plant, Though enzyme usage as bleach boosting agent has been widely discussed in recent past, it's commercial viability was

yet to be fully established. Based on the successful pilot scale studies conducted, Century Pulp and Paper adopted the new technology for its different fibre lines for varying durations to good effect and has been able to establish an ECF bleaching sequence for it's Bagasse based plant.

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ENZYME PREBLEACHING

A close interaction and further studies in collaboration with supplier has resulted in development of an improved enzyme product that requires lower dosage without affecting the cost and quality of the treatment process.

Century Pulp and Paper is an integrated pulp and paper unit having three fibre lines with installed capacities of 31320 TPA Rayon Grade Pulp, 37250 TPA Writing and Printing paper based on Eucalyptus and 84600 TPA Bagasse based paper plant.

Annexure : I

Effect of Enzyme on bleachability of WPP pulp under different conditions

Unbleach pulp Kappa No. : 18.84
 Brightness % : 34.4
 Viscosity cP : 12.7

(0.5% CED Soln.)

Effect of pH

Set No	I	II	III	IV	V
Pulp Consistency %	10	10	10	10	10
Enzyme Doses gm/tonne	X	500	500	500	500
Retention Time, mints	60	60	60	60	60
Temperature °C	Ambient	Ambient	Ambient	Ambient	Ambient
pH	8.0	6.0	7.0	8.0	9.0
Kappa No.	18.84	18.0	18.64	17.28	17.06
Brightness %	34.4	35.2	35.0	35.2	35.4
Viscosity cP	12.7	13.6	13.55	13.4	13.2

(0.5 % CED Soln.)

Effect of Doses

Set No	I	II	III	IV	V
Pulp Consistency %	10	10	10	10	10
Enzyme Doses gm/tonne	300	400	500	600	700
Retention Time, mints	60	60	60	60	60
Temperature °C	Ambient	Ambient	Ambient	Ambient	Ambient
pH	8.5	8.5	8.5	8.5	8.5
Kappa No.	17.93	17.39	16.92	16.40	16.24
Brightness %	35.0	34.7	35.3	34.9	35.4
Viscosity cP	13.9	13.7	13.7	13.6	13.5

(0.5 % CED Soln.)

Effect of Temperature

Set No	I	II	III	IV	V
Pulp Consistency %	10	10	10	10	10
Enzyme Doses gm/tonne	500	500	500	500	500
Retention Time, mints	60	60	60	60	60
Temperature °C	Ambient	40	50	60	70
pH	8.5	8.5	8.5	8.5	8.5
Kappa No.	16.92	16.72	16.64	17.12	17.44
Brightness %	35.3	35.3	35.1	35.0	35.0
Viscosity cP	13.7	14.3	14.05	14.0	14.05

(0.5 % CED Soln.)

BACKGROUND

During the bleaching process, a significant amount of Organic material is dissolved in Chlorination and Extraction stage. When Chlorine is extensively used for bleaching, an appreciable quantity of Organically bound Chlorine finds its way in the effluent, reported as Adsorbable Organic Halides (AOX). In view of the proposed revision of the limit for this parameter, it becomes imperative that necessary corrective steps are taken to minimise this load.

Enzyme Pre bleaching using Xylanase enzymes offers a solution by improving the effectiveness of conventional Bleaching chemicals in removing Lignin. Xylanase enzymes are reported to partially hydrolyse

the hemi-cellulase portion of pulp. The enzyme is presumed to hydrolyse Xylan into smaller fragments allowing lignin associated with these short hemi-cellulose chains to be more easily removed through subsequent Extraction stages in bleaching.

EXPERIMENTAL

Detailed experimentations with both Wood and Bagasse pulps were conducted to ascertain the effectiveness of bleach boosting enzyme. During the lab studies, effect of Pulp Consistency, Retention Time, Enzyme Dosage, Temperature and pH were particularly monitored and optimised. The effect of these parameters on unbleached pulp (WPP) are depicted in Annexure I based on which the optimal Conditions were found as ;

Annexure : II

Bleaching of Enzyme treated pulp

Bleaching Sequences :

Set No	I	II	III	IV	V
	Nil	Enzyme	Enzyme	Enzyme	Enzyme
	C / D	C / D	C / D	C / D	C / D
	E / P	E / P	E	E / P	E
	Hypol	Hypol	Hypol	Hypol	Hypol
	HypolII	HypolII	HypolII	---	---
	D	D	D	D	D
	SO ₂	SO ₂	SO ₂	SO ₂	SO ₂

Properties

Brightness (ISO)	% :	86.7	87.7	87.2	87.6	88.15
P. C. No	:	0.23	0.21	0.21	0.19	0.16
Yellowness	% :	4.67	3.86	3.87	3.49	3.45
L	:	96.47	96.09	95.69	95.60	96.42
a	:	- 0.4	- 0.4	- 0.4	- 0.4	- 0.4
b	:	2.6	2.2	2.1	2.0	2.1
Viscosity (0.5% CED Soln.)	cP :	3.94	4.07	4.26	4.55	4.70

Addition of Chemicals and Conditions (Bleaching)

	C / D	E / P	Hypol	HypolII	D	SO ₂
Chemical	% :	3.0	2.0	2.0	0.5	0.19
		0.15	0.5			
Retention Time	mins :	45	90	90	90	180
Temp.	°C :	Ambient	60-65	40-42	40-42	70-75 Ambient

Annexure : III

**Bio Bleaching of Bagasse Pulp
Unbleach pulp sample collected from unbleach thickner**

Condition of Enzyme Treatment :

	Doses :	0.05 %	
	Retention time :	60 mints	
	Temp :	Ambient	
	pH :	8.5	
	As such		After Enzyme Treatment
Kappa No.	:	10.98	9.54
Brightness	% :	49.60	50.10
Viscosity	cP :	20.98	21.76

**Bleaching Experiment
Set No.**

	Without enzyme Treatment.	Enzyme Treated Pulp						
	 * Normal	 * ECF	 * ECF	 * ECF	 * ECF	 * ECF	 * ECF	 * ECF
	I	II	III	IV	V	VI	VII	VIII
	C/D	D	D	D	D	D	D	D
	E/P	E/P	E/P	E/P	E/P	E/P	E/P	E/P
	D	D	D	D	D	D	D	D
	SO ₂	SO ₂	SO ₂	SO ₂	SO ₂	SO ₂	SO ₂	SO ₂
Chemical Additions :								
Ist Stage								
Cl ₂ % :	2.0	-	-	-	-	-	-	-
ClO ₂ % :	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
H ₂ SO ₄ % :	--	0.5	0.5	0.5	0.5	0.5	0.5	0.5
IInd Stage								
NaOH % :	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
H ₂ O ₂ % :	0.5	0.5	0.5	0.5	0.75	0.75	1.0	1.0
IIIrd Stage								
ClO ₂ % :	0.5	0.5	0.5	0.5	0.7	0.5	0.7	0.7
H ₂ SO ₄ % :	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
SO ₂ % :	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Br. % :	88.1	84.7	85.9	86.8	85.4	86.7	86.8	87.8
(ISO)								
P. C. No. :	0.1	0.48	0.34	0.27	0.29	0.24	0.21	0.19
Vis. cP :	17.6	16.90	17.2	16.9	17.2	17.4	17.5	17.3
(0.5% CED)								
Yell. % :	2.49	4.79	3.97	3.90	3.79	3.80	2.96	2.70

	Retention time (Mints)	Temp. (°C)	pH
	Normal / ECF	Normal / ECF	Normal ECF
Ist Stage :	45	Amb. 50-55	2.1 3.7
IInd Stage :	120	60-65	9.6 9.7
IIIrd Stage :	180 150	70-75	3.8 3.9

Yellowness (Yell.) reduced and brightness (Br.) stability improves with H₂O₂ treatment while brightness improve with ClO₂ treatment.

Annexure : IV

Bio Bleaching : Dissolving Grade Pulp.

Unbleach pulp sample collected from unbleached thickner (RGP)

Condition of Enzyme Treatment :

	Doses :	0.05 %	
	Retention time :	60 mints	
	Temp :	Ambient	
	pH :	8.5	
		As such	After Enzyme Treatment
Kappa No.		12.62	11.52
Brightness % :		32.1	33.90
Viscosity cP :		10.6	10.80

Bleaching condition

- Three set were conducted for bleaching
a: Without enzyme treatment (Normal sequence)
b: With enzyme treatment (Normal sequence)
c: With enzyme treatment (Hypo II eliminated)

Bleaching Sequences :

		<u>C</u>	<u>E</u>	<u>HypoI</u>	<u>HypoII</u>	<u>Dioxide</u>	<u>SO₂</u>
Chemical	% :	3.2	2.8	2.0	0.5	1.0	0.40
Retn. Time, Mints	:	60	90	90	90	180	30
Temp.	°C :	Ambient	60-65	40	42	75 -80	Ambient

Properties (Final Pulp) :

		Set No. I	Set No II	Set No III
		(a)	(b)	(c)
Brightness	% :	87.10	88.70	88.6
(ISO)				
Yellowness	% :	3.93	3.78	3.41
P.C. No	:	0.79	0.42	0.3
Viscosity	cP :	4.7	5.1	4.9
(0.5% CED Soln.)				

Consistency : 10%
Retention Time : 60 minute.
Temperature : Ambient
pH : 8.5

These conditions were tailored to suit the existing process facilities. Enzyme treated pulp was further bleached under various sequences to attain a brightness of 87.0% (+). The details of the bleaching and the

findings are shown in Annexure II. An increase in brightness by 1.5 points even after elimination of Hypo II stage was achieved, with reduction in yellowness and P.C. No.

For Bagasse pulp, attempts were made to achieve the required brightness by totally eliminating Elemental Chlorine (ECF) by supplementation with Hydrogen peroxide in the Extraction stage.

The experimental details on the Bleachability of Bagasse Pulp with and without enzyme and further

**Annexure : V
Bio Bleaching with Improved Version Enzyme
(W P P Pulp)**

Unbleach pulp sample collected from unbleach thickner

Condition of Enzyme Treatment :

Doses gm/tonne :	200	250	300
Retention time :	60 mints		
Temp :	Ambient		
pH :	8.5		
As such	<----	After Enzyme Treatment	---->
Blank	200	250	300
Kappa No. :	19.43	17.64	17.50
Brightness % :	26.5	26.9	26.8
Viscosity cP :	13.0	13.4	13.5

Bleaching Experiment

	<----- Enzyme Treated Pulp ----->				
	Blank	200 gm	300 gm	200 gm	
Set No :	I	II	III	IV	(Chemical Addition)

	C / D	C / D	C / D	C / D	2.0 + 0.15
	E / P	E / P	E / P	E / P	2.0 + 0.5%
	Hypol	Hypol	Hypol	Hypol	2.0 %
	HypolII	HypolII	HypolII	---	
	D	D	D	D	0.5 %
	SO ₂	SO ₂	SO ₂	SO ₂	0.2 %
Brightness % :	84.35	85.89	86.14	85.66	
(ISO)					
P. C. No :	0.77	0.36	0.33	0.46	
Viscosity cP :	5.85	5.97	5.92	5.89	
(0.5 % CED)					
Yellowness % :	7.70	5.76	5.42	5.86	

Addition of Chemicals and conditions (Bleaching)

(***) Except set No IV)

	C/D	E/P	Hypol	HypolII	D	SO ₂
Chemical % :	3.0	2.0	2.0	0.5	0.5	0.19
	0.15	0.5				
Retention Time mints :	45	90	90	90	180	15
Temp. °C :	Ambient	60-65	50-----	55	75-80	Ambient

supplementation with chlorine-Dioxide and Hydrogen Peroxide is as per Annexure III attached.

Similar studies with dissolving grade Pulp (Eucalyptus) fibre line are shown in Annexure IV attached.

As part of the recent development based on the

detailed experimentation on pilot and Plant scale, an improved version of the Enzyme Product has been developed with appreciable reduction in dosage i.e. from 500 gm/T to 300 gm/T without any effect on cost/quality. The details on this product are shown in Annexure V. as conducted on WPP (Wood based) fibre line. Further studies have been planned to try this product on wood based pulping section.

Table : 1
Plant trial details of Enzyme Prebleaching in WPP Street

Particulars		Without	With Enzyme	
		Enzyme	I	II
	Unbleached Pulp			
Enzyme	gm/T	0	500	500
Temp	°C	Ambient	Ambient	Ambient
Retention time	min.	60	60	61
pH		8.0-9.0	8.0-9.0	8.0-9.0
Kappa No.		19.1-22.5	17.0-18.8	16.6-19.3
Chlorine/Dioxide stage				
Cl ₂	%	2.5	2.5	2.5
ClO ₂	%	0.34	0.34	0.34
pH		2.0-3.0	2.0-3.0	2.0-3.0
Kappa No.		9.8-11.9	6.8-7.3	6.7-7.6
Alkali Extraction/Peroxide Stage				
NaOH	%	1.1	1.1	1.1
H ₂ O ₂	%	0.5	0.5	0.5
pH		9.5-10.5	9.5-10.5	9.5-10.5
Kappa No.		8.0-9.3	4.9-5.3	4.7-5.6
Hypo I Stage				
Hypo (as Cl ₂)	%	2.3	2.3	1.88
pH		8.0-9.0	8.0-9.0	8.0-9.0
Hypo II Stage				
Hypo (as Cl ₂)	%	1.75	1.75	0.66
Brightness	%	82.3-83.4	83.0-84.5	83.1-84.3
pH		7.5-8.0	7.5-8.0	7.5-8.0
Chlorine Dioxide Stage				
ClO ₂	%	0.2	0.2	0.2
pH		3.0-5.0	3.0-5.0	3.0-5.0
Brightness	%	84.5-85.3	86.0-86.8	86.0-86.5
Viscosity (0.5CED)	cP	4.0-4.44	4.9-5.1	5.05-5.15
PC No.		1.0-1.14	0.5-0.69	0.44-0.62
Yellowness	%	5.17-6.39	2.9-4.0	2.6-3.9
Strength Properties at 35 °SR				
Burst Factor		31	30	30
Tear Factor		50	48	54
Breaking length (meters)		4890	5070	5120
Double Fold (No.)		18	15	17
In set-II, Hypo II was eliminated and Hypo-In splitted in two stages				
@ 80:20 ratio.				
Additional Cost Rs/T			350	200
of Chemicals				

Table : 11
Plant trial details of Enzyme Prebleaching in Bagasse Street

Particulars	Without		----- With Enzyme -----		
	Enzyme		I	II	III
				ECF	ECF
Unbleached Pulp					
Enzyme gm/T	0	500	500	500	500
Temp. °C	Ambient	Ambient	Ambient	Ambient	Ambient
Retention time, min.	60	60	60	60	60
pH	8.0-9.0	8.0-9.0	8.0-9.0	8.0-9.0	9.0-9.0
Kappa No.	11.4-13.6	9.84-11.14	9.04-10.56	9.12-10.8	
Chlorine/Dioxide stage					
Cl ₂ %	2.2	1.5-1.6	0	0	0
ClO ₂ %	0.14	0.12-0.14	0.46	0.46	0.46
pH	1.0-1.8	1.5-2.0	1.5-2.0	1.5-2.0	1.5-2.0
Kappa No.	4.0-4.73	3.2-4.98	3.2-5.28	2.56-4.48	
Brightness %	56-61	58-62	59-64	58-66	
Alkali Extraction/Oxygen Stage					
NaOH %	1.5	1.48	1.0-1.27	1.2	
O ₂ %	0.4	0.4	0.4-0.5	0.4	
H ₂ O ₂ %	0	0	0	0.27	
pH	9.5-10.5	9.5-10.5	9.5-10.5	9.5-10.0	
Kappa No.	1.19-1.68	1.2-1.84	0.96-1.42	0.72-1.60	
Brightness %	68-72	67-72	74-78	75-85	
Chlorine Dioxide Stage					
ClO ₂ %	0.46	0.46	0.45-0.48	0.49	
pH	3.0-3.0	2.0-3.0	2.0-3.0	2.0-3.0	
Brightness %	86.6-68.0	86.4-88.0	87.5-89.5	88.2-90.2	
Viscosity (0.5 CED) cP	11.8-12.7	13.75-17.79	17.79-18.0	16.98-18.93	
PC No.	0.24-0.42	0.16-0.30	0.12-0.30	0.12-0.30	
Yellowness %	1.52-2.0	1.03-1.8	1.0-1.76	0.45-0.76	
Strength Properties at 35 °SR					
Burst Factor	30	31	32	32	
Tear Factor	53	53	50	49	
Breaking length (meters)	4980	4880	5050	5230	
Double Fold (No.)	14	19	18	15	
Additional Cost Rs/T of Chemicals	-	295	345	415	

RESULTS AND DISCUSSION

Based on the encouraging trends of pilot scale findings, Plant scale trials were undertaken. Enzyme was dosed at out let of Unbleached thickner @ 500 gm/

T after dilution. On line dilution arrangement was made as enzyme in diluted form is reported to be unstable. Retention time of at least 60 minutes and proper mixing with pulp are another factors considered for optimum results.

Table : III

S. No.	Particulars	AOX Levels in Effluents		% Reduction
		Normal	Enzyme Treated	
1	Writing Ptg Paper (Wood Based) (Bleach Effluent)	2.39	1.37	42.6
2	Bagasse Plant (Bleach Effluent)	1.28	1.07	16.4
3	Final Discharge	0.96	0.84	12.5

Results based on analysis carried out by out side agencies.
CPP in the process of equipment procurement)

For Wood based fibre line during a month long trial maintaining the same bleaching chemicals, a Brightness improvement of 1.5 points was achieved. Further, Hypo II stage was eliminated i.e. 1.75% dose of Chlorine without affecting the quality of pulp. There was reduction in yellowness and P.C. Values. The details of the process conditions and results obtained are given in Table No.1

During the plant scale trials in bagasse bleaching , brightness could be maintained at the control levels with reduction of Chlorine to the tune of 7 kgs per tonne. Further experimentations by totally eliminating Chlorine with increased dosage of Chlorine dioxide and in second phase, introduction of Hydrogen Peroxide resulted in establishment of an ECF bleaching sequence with improved quality pulp.

Appreciable reduction in P.C. No./Yellowness was noticed. The detailed findings of the month long trial in Bagasse based fibre line are given in Table No. 2.

Samples of effluent discharge from the bleach plants as well as the final discharge from the mills were got analysed by the recognised outside laboratories. Appreciable reduction in terms of AOX was indicated. Company is in the process of procuring the necessary equipments for in-house testing of AOX.

The findings of blank vis-a-vis enzyme treated pulp w.r.t. AOX levels is given in Table No. 3. Though the Bleach plant effluents could not be separately investigated for B.O.D./C.O.D. loadings, no change

was noticed in the final effluent discharge w.r.t. these parameters. Detailed studies for these will be undertaken during the next runs with enzyme.

ECONOMICS

The additional chemical cost of Enzyme Pre-bleaching in case of wood based pulping comes to around Rs. 200/- per ton and in case of Bagasse with "ECF" in the range of Rs. 345-415 per tonne which is expected to be at par incase of WPP and around Rs. 135-205 in case of Bagasse respectively if the new version of the product dosage @ 300 gms per tonne is established on the Plant scale.

The intangible gains in terms of improved products quality and appreciable reduction in AOX levels are not quantified.

CONCLUSION

Bio Bleaching followed by Peroxide bleaching stage offers an affordable ECF bleaching system. Elimination of Elemental Chlorine from the Bleach plant without sacrificing on the pulp quality or any increase in the cost is feasible by incorporating Enzyme treatment.

In longer terms, this approach will gain paramount importance when pressure on limiting the Chlorinated organic compound in the effluents will rise. With optimisation of dosage and process conditions, Biobleaching could be a cost effective, viable technology for the Pulp and Paper Industry.

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