Enzymatic Treatment on Chemical Pulp in Beating/ Refining Process– An Attempt Towards Energy Conservation.

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In India pulp and paper industry is the sixth largest energy consumer in the industrial sector and it's energy costs account for about 25% of the total manufacturing cost. For the development of required pulp properties, beating and refining require substantial energy, about 18% of the total electrical energy. A beating/refining study was carried out in laboratory using different enzyme cellulase/hemicellulase (carbohydrase enzyme) on unbleached and bleached mixed (hardwood + bamboo) chemical pulp. The results of lab study shows; there is increase in freeness value up to 5 °SR at the fixed time of beating with the pre-treatment of enzyme on pulp at the dose of 200gm/MT of OD pulp. There is reduction in beating time at the same level of freeness °SR to an extent of 20%. To validate lab study & considerations of enhancing both economic and ecological efficiency, a full-scale mill trail was conducted on the fourdrinier paper machine of 350m/min speed manufacturing writing/printing paper. There was reduction in the energy used in refining of pulp by 15-20% with the dose of enzyme @ 30g/MT of OD pulp while maintaining the same freeness (28 °SR) level & strength properties of paper.

INTRODUCTION

The pulp and paper industry is applying new, ecologically sound technology in its manufacturing processes. Many interesting enzymatic applications have been proposed in the literature. Implemented technologies tend to change the existing industrial process as little as possible. Commercial applications of enzyme include xylanase in pre-bleaching of kraft pulps, and various enzymes in beating/refining process & recycling paper [1,2]. Enzymes are very large, complex protein molecules consisting of intertwined chains of amino acids. They are formed within the cells of all living creatures, including humans, animals, plants, fungi, bacteria, and microscopic single cell organisms. [3].

Enzymes control many vital functions such as the metabolic processes, which convert nutrients into energy and they are highly efficient at increasing the reaction rate of biochemical processes. Each enzyme has a highly specific target, breaking down or synthesizing certain compounds, and operating under specific temperature, pH and retention time [3,13]. Commonly used enzymes include lipases, which split fats into glycerol and fatty acids; amylases, which break starch down to produce simple sugars; proteases, which break down proteins; and cellulase, which break down cellulose [3].

An enzyme (E) molecule has a highly specific binding site or active site to which its substrate (S) binds to produce enzyme-substrate complex (ES). The reaction proceeds at the binding site to produce the products (P), which remains associated briefly with the enzyme (enzyme product complexes) EP. The product is then liberated and the enzyme molecules are freed in an active state to initiate another round of catalysis as depicted in the following equation. Apparently, the affinity of binding site for the product is much lower than that for the substrate [4].

 $E+S \leftrightarrow ES \leftrightarrow EP \leftrightarrow E+P$

MECHANISM OF ENZYME IN REFINING

Pulp refining is a mechanical treatment of fibers to develop their optimum papermaking properties, which depends on the product being made [5]. The primary effects of beating/refining on fibers are considered to be external fibrillation, internal fibrillation, production of fines and fiber shorting [6]. Refining increases the strength of fiber-to-fiber bonding by increasing the surface areas of the fibers [5].

Enzyme treatment of pulp modifies the pulp properties such as improved fiber flexibility and fibrillation (internal & external) both [7]. Enzyme helps to soften the fiber walls and increase access to cellulose fibers and breaking the primary wall, which is thin (0.05 micron thick) & relatively impermeable. It helps in the S1 peeling process (as S1

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layer 0.1-0.2 micron thick is the outer layers of secondary). Fiber becomes easier to refine with the addition of enzyme and digest small fiber fraction, reducing fines [8]. Enzyme treatment requires additional retention time and sufficient mixing to affect the fiber surface. Desired results can be achieved at optimum pH, temperature and with appropriate mixing [5].

REASON FOR USE OF CARBOHYDRASE ENZYME

The principle challenge in using enzyme to enhance fiber bonding is to increase fibrillation without reducing pulp viscosity. Viscosity decreases when cellulases cleave cellulose chains, lowering the degree of cellulose polymerization (number of glucose residues per chain) and destroying fiber integrity. In one attempt to get around this problem, researcher fiberized pulp using "cellulose-free" xylanase. Xylanase enzyme treatments removed less than 2% of the total weight while improving fibrillation and fiber bonding and decreased beating times. This increased freeness (SR) value, and the water retention value. However, at the same time it decreased viscosity, and decreased breaking length drastically [9, 12]. Both of these negative effects of cellulase and xylanase enzyme, we have selected combination of cellulase/ hemicellulase (carbohydrase) enzyme in the lab study and plant trial.

Cellulase/hemicellulase formulation enhances and restores fiber strength; reduce refining energy requirements and increases inter-fiber bonding fibrillation, while increasing drainage rates and avoiding fiber breakage [3,13]. A minor part of the carbohydrates in order to improved processes and products for the pulp and paper industry. Cellulose is the major component in all pulp and paper products, which is chemically one of the simplest carbohydrates, consisting of only 1-4 linked glycosyl units. The site of action of enzyme depends on the accessibility of the substrate, and thus the chemical pulps, having larger average pore sizes are generally considered as more accessible substrates for enzymatic attack [10,11].

EXPERIMENTALAPPROACH

A laboratory scale study was conducted on unbleached and bleached chemical pulp (Hardwood + Bamboo) using two different enzymes with the following objectives.

- Effect on freeness/drainage & strength properties – to remove bottleneck during refining in the process
- Effect on beating time to save energy during beating/refining in the process.

We have studied two different enzymes in the laboratory to select effective one for process trial.

Unbleached pulp was collected from the final stage of the brown stock washer and bleached pulp from bleached Decker after centricleaner. Mixed pulp have the furnish bamboo 15%, eucalyptus 15%, popular 20% & veneer waste 50%. On fiber morphology study of bleached pulp [figure1], fiber length varied from 0.5 to 3.5 mm average being 1.2 mm and diameter varied from 11 to 35 micron average being 22 micron. Two different enzyme of cellulase/ hemicellulase (carbohydrase) were used in laboratory. Enzyme treatment was given to the pulp at pH 6.5-6.8, Cy 5.0%, and temperature of 50°C with the retention time 1.0 hrs.



Figure I. Effect on fiber with and without enzymatic treatment on bleached pulp.

I. Effect on freeness/drainage & strength properties

Enzymatic treatment was given before beating at conditions given above at the dose of 200gm/MT of OD pulp. Beating was carried out in valley beater with maintaining the same beating time i.e. 45 min. enzyme-1& 2 on both (unbleached & bleached) pulps. Hand sheets of 60gsm were made on British Hand Sheet Machine at neutral pH 6.8-7.0 with unbleached & bleached beaten pulps. The hand sheets were pressed and then air-dried. Hand sheets were conditioned at the standard humidity 65±2% and temperature 27±1°C and then tested for various properties as per the standard*. Results are tabulated in [Table 1] & [Table 2]. *Standards used (Burst factor T 403 om-02, Breaking length T 456 om-03, Tear factor T 414 om-98, Double fold SCAN-P17:17, Brightness T 571 om-03, Opacity T 519 om-02, Gurley porosity T 460 om-02, Water Cobb T 441 om-98, Wax pick T459 om-03, Smoothness SACN-P 84: 02).

II. Effect on beating time

The unbleached & bleached pulps were given enzymatic pretreatment at the dose of 200gm/MT of OD pulp at 5.0% consistency, retention time 60 min at 50°C temperature. The unbleached & bleached pulps (control & treatment) were then beaten in valley beater at the same freeness level i.e. 28 °SR. Hand sheets were also made at British Hand Sheet Machine at neutral pH 6.8-7.0 for the evaluation of their strength properties. The hand sheets were pressed, air-dried and conditioned at the standard humidity 65±2% and temperature 27±1°C before testing for strength properties as per the standard*. The results are given in [Table 3] & [Table 4]. Power consumed in lab valley beater checked by the instrument of Meco 4500 clamp meter (range 0-2000kW).

PLANT TRIAL

We have achieved the superior results in regards to beating time (energy saving) and improvement in the strength properties in laboratory trial with the pre-treatment of both the pulps with enzyme-2. To validate the laboratory results a full-scale plant trial

Table 1. Effect of enzymatic treatment on freeness/drainage
and strength properties of unbleached pulp

Table 2. Effect of enzymatic treatment on freeness/drainage & strength properties of bleached pulp

Parameters	1(control)	2(ET)	3(ET)	Parameters	1 (control)	2(ET)	3(ET)
Enzyme treatment*				Enzyme treatment*			
Name of enzyme	-	Enzyme-1	Enzyme-2	Name of enzyme	-	Enzyme-1	Enzyme-2
Initial pH	-	6.65	6.70	Initial pH	-	6.60	6.70
Final pH	-	6.75	6.85	Final pH	-	6.70	6.80
Beating				Beating			
Consistency, %	1.54	1.52	1.52	Consistency, %	1.56	1.59	1.54
Beating time, min.	45	45	45	Beating time, min.	45	45	45
Initial ^o SR	15	16	16	Initial °SR	16	17	18
Final °SR	28	30	32	Final °SR	32	35	37
30 second drainage, ml	74	70	66	30 second drainage, ml	70	63	62
Drainage time for 800 ml, sec.	8.5	9.0	10	Drainage time for 800ml so	. 74	05 05	02
Hand sheet property				Dramage time for soonin, se	L. 7.4	0.5	9.5
Bulk, cc/g	1.40	1.40	1.39	Hand sheet property			
Burst Factor	44.0	45.0	45.5	Bulk, cc/g	1.38	1.38	1.36
Breaking Length, meter	6460	6510	6700	Burst Factor	45.0	45.5	46.5
Tear Factor	76.4	77.0	77.5	Breaking Length, meter	6680	6810	6950
Double Fold, nos.	131	140	152	Tear Factor	65.8	67.0	68.0
Gurley Porosity, sec/100ml	45.5	49.4	52.4	Double Fold, nos.	104	110	120
*Enzyme treatment conditions: Enzyme dose 200 gm/MT,			Gurley Porosity, sec/100m	1 46.4	50.1	54.5	
consistency 5.0%, temp. 50 °C, retention time 60 min. ET=			*Enzyme treatment conditions: Enzyme dose 200 gm/MT,				
Enzyme treatment			consistency 5.0%, temp. 50 °C, retention time 60 min. ET=				
Hand sheets were conditioned before testing at 65±2% RH &			Enzyme treatment				
27±1 °C temp.			Hand sheets were conditioned before testing at $65\pm2\%$ RH &				
-				27±1 °C temp			

Table 3. Effect on beating time in unbleached	pulr	n
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Table 4. Effect of beating time in bleached pulp. Parameters 1 (control) 2(ET) 3(ET) Parameters 1 (control) 2(ET) 3(ET) Enzyme treatment* Enzyme treatment* Name of enzyme Enzyme-1 Enzyme-2 Name of enzyme Enzyme-1 Enzyme-2 Initial pH 6.60 6.70 Initial pH 6.60 6.65 Final pH 6.65 6.75 _ Final pH 6.70 6.80 Beating Beating Consistency, % 1.55 1.56 1.55 Consistency, % 1.55 1.56 1.55 Beating Time, min. 35 32 30 Beating time, min. 35 30 27 Power consumed kWh 0.233 0.213 0.200 Power consumed kWh 0.233 0.200 0.180 Hand sheet properties Hand sheet properties Bulk, cc/g 1.38 1.37 1.38 Bulk, cc/g 1.37 1.37 1.36 Burst factor, cc/g 40.0 40.5 40.5 Burst factor, cc/g 40 40.5 40.5 Breaking length, meter 6480 6470 6490 Breaking length, meter 6850 6860 6860 Tear factor 77.5 77.4 78.0 Tear factor 72 71 72 Double fold 50 52 51 Double fold. No. 38 40 41 Gurley porosity, sec/100 ml35 35 38 Gurley porosity, sec/100 ml30 28 29 *Enzyme treatment conditions: Enzyme dose 200 gm/MT, *Enzyme treatment conditions: Enzyme dose 200 gm/MT, consistency 5%, temp. 50 °C, retention time 60 min. ET= consistency 5.0%, temp. 50 °C, retention time 60 min. ET= Enzyme treatment, Enzyme treatment, Hand sheets were conditioned before testing at 65±2% RH & Hand sheets were conditioned before testing at 65±2% RH & 27±1 °C temp 27±1 °C temp

was conducted for 3 days on the fourdrinier paper machine, speed of 350m/min, deckle 3.15m, manufacturing the writing & printing paper in different gsm 54 to 80. We are generally maintaining a freeness value of 28°SR after refining at stock preparation. In this trial focus was given to reduce the refining energy by maintaining the same freeness value of 28°SR.

Wet end condition

Pulp was received from the pulp mill at the consistency of 3.0-3.5%. Pulp was first taken on the thickener and then stored in the buffer chest. Retention time in this chest is about 2.0 hrs. The pulp characteristics was as follows; viscosity 10.0 cps, brightness (ISO) 89.0%, FLI (Fiber length index) 0.35. Enzyme -2 was added in the buffer chest (addition point shown in Figure-2) at the rate of 50 gm/MT of OD pulp and retention time of 2 hrs was given at temperature of 35 °C and pH of 6.7. After 24hrs, dose of enzyme was reduced 30 gm/MT of OD pulp. Pulp was refined in the DDR (make L&T). During trial, we had fixed the refining level i.e. 28 °SR of pulp so that we can achieve the gain of power saving consumed in refining. Refiner load reduced to 22amp from the normal 27amp in enzyme treated pulp to maintain the same freeness level. Refining conditions are given in [Table 5].

Bilt classic paper in 60 gsm was manufactured at fourdrinier paper machine at a speed of 350m/min. Paper was tested for various properties after conditioning in controlled room (RH 65 $\pm 2\%$ & temp $27\pm 1.0^{\circ}$ C). Before commencement of the trial, 2 days control data (without enzyme) was collected and tabulated in [Table 6] along with the trial results (treated).

Table 5.	Enzyme-2	treatment	in	refining	of	pul	lp
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Parameters	1 (control)	2(ET)			
Name of enzyme*	<u>-</u>	Enzyme-2			
Initial pH	-	6.70			
Final pH	-	6.90			
Refiner, DDR					
Consistency, %	3.52	3.51			
Refiner load amp	27	22			
Initial °SR	17	17			
Final °SR	28	28			
Energy consumed in refiner kWh	262	213			
* Enzyme treatment conditions: Enzyme dose 30 gm/MT, consistency 3.5%,					
temp. 35 °C,					
retention time 120 min. ET= Enzyme treatment					

Table 6. Test results of 60 gsm paper and compared with the enzyme & normal run (control).

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Parameters		1 (control)	2(ET)	
Name of enzyme		-	Enzyme-2	
Substance, g/m ²		60	60	
Thickness, micron		80	81	
Bulk, cc/g		1.35	1.35	
Burst factor		29.4	29.1	
Baking length, meter	MD/CD	6200/3150	6190/3100	
Double Fold, no.	MD/CD	30/18	30/20	
Tear Factor, MD/CD		54/60	55/60	
Brightness (ISO), %		88.4	88.5	
Opacity ISO, %		84.5	84.4	
Cobb, g/m ²	Top/wire	19/21	19/21	
Wax pick	no.	13A	13A	
Smoothness, ml/min	Top	70-150	80-150	
Bendtsen	Wire	90-200	90-200	
Formation Index		140-150	140-150	

All test results are comparable with the normal run paper. ET= enzyme treatment Control data (normal run) are the average of 12 values and trial data are the average of 18 values. Calculation for power saving



Fig 2. Approach flow system

Case (I) Untreated pulp (control) Load at refiner = 27 ampPower consumed in refiner = 262.34kWh Case (II) Treated pulp Load at refiner= 22 amp Power consumed in refiner = 213.76kWh Power saving = 262.34 - 213.76 = 48.58kWh Machine draw= 3.5 MT/hr Power saving MT of paper = 13.9 kWhPower saving in Rs. per MT= Rs. 30.5 (power cost Rs. 2.20 / kWh) Enzyme cost in Rs. per MT = Rs. 16.1 (Rs. 537 / kg, at dose 30gm) Saving in Rs. per MT= Rs. 14.4

RESULTS AND DISCUSSION

Laboratory trial

At the constant beating time, there was improvement in freeness value by 2 & 4 °SR point on unbleached pulp with the treatment of enzyme 1 & 2 respectively [Figure 3] while with the bleached pulp freeness level improved by 3 & 5 °SR point with the treatment of enzyme 1 & 2 respectively [Figure 4] at the enzyme dose of 200 gm/MT of OD pulp. Viscosity of pulp remained more or less same with the treatment. Breaking length improved maximum with the treatment of enzyme-2 i.e. 6460 to 6700 meter with unbleached [Figure 5] and 6680 to 6950 meter with bleached pulp [Figure 6].

For the freeness level i.e. 28 °SR, beating time was reduced from 35 to 32 & 30 min with the treatment of enzyme-1 & 2 respectively with the unbleached pulp. With the bleached pulp, beating time was reduced from 35 to 30 & 27 min with enzyme-1 & 2 respectively. The dose of the enzyme was similar i.e. 200gm/MT of OD pulp.

There was reduction in beating time by 8.6% & 14.3% in unbleached pulp with the treatment of enzyme 1 & 2 respectively. Similarly with the bleached pulp, beating time reduced by 14.3% & 22.8% with the treatment of enzyme 1 & 2 respectively. Enzyme -2 performed better than the enzyme-1. Due to higher reduction in beating time with enzyme-2, the process trial was conducted with the enzyme-2.

Plant trial

We have fixed the freeness value i.e. 28 °SR and reduced the load at DDR refiner i.e. 22amp from the 27amp at the dose 30gm/MT on OD pulp of enzyme-2. All paper properties i.e. physical, strength, optical and surface properties were comparable with the control run (untreated). There is reduction in power consumption during refining by 18.5% (262 kWh to 213 kWh) with the application of enzyme.

CONCLUSION

Enzyme performs better in the bleached pulp as compare to unbleached chemical pulp. Enzymatic pretreatment



Fig. 3. Effect on freeness (°SR) of enzyme treatment in unbleached pulp







of chemical pulp in laboratory, has resulted increase in freeness value (°SR) by 5 point in bleached pulp. Breaking length improved up to 4.0% at the constant beating/refining.

There is reduction in beating time with the application of enzyme. There are 18.5% energy saving during refining of pulp at plant maintaining the same paper properties at constant refining level i.e. freeness 28 °SR. There is saving of Rs. 14.4 per MT of paper. This is the step towards conserving the natural resources i.e. energy conservation. It has been commercialized.

FUTURE ASPECTATION

With rising power cost and possible reduction in enzymes cost in the near future, this process seems to have more potential. For a better understanding of the enzyme effects on fibers to emerge, there is need for details study in the development of cost effective enzyme in the energy conservation.

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