

Improvement in Pulp Dewatering Through Cellulases

Verma Piyush¹, Bhardwaj N. K.², Singh S. P.¹

ABSTRACT

Enzymatic processes provide a natural solution for various problems encountered in the papermaking process. Studies have shown that a judicious choice of the enzyme component, its dosage, point of addition and the duration of treatment can help to achieve significant freeness increase, while avoiding degradation to the fibres.

Cellulases have been studied for improved paper recycling since the 1980s. Secondary pulp contains great amount of fines having high relative surface area, therefore these fibers adsorb water to large extent. This effect of fines is enhanced by microfibrils and colloidal layer located on the surface. Thus dewatering rate on wire section is lower compared to virgin pulp. The result is considerably decreased productivity of the paper making process compared to operation using virgin pulp. Productivity of paper processing can be significantly increased through improvement of pulp drainage.

This paper covers the understanding whether the effectiveness or strength loss depends on a specific type (EG or CBH) of enzyme activity. Interestingly, in the experiments carried out, the increased solubilization of amorphous cellulose mediated by endoglucanase treatments consequently improved drainability.

Key words: Recycled pulp, pulp properties, drainage, dewaterability, enzymes, endo/exo cellulase

Introduction

Paper recycling offers several advantages; substitution of virgin pulp with recycled pulp saves wood for making pulp, which reduces the exploitation of forests important for the biodiversity. Several problems are also associated with the recycling of waste paper. These are deinking of different types of post consumer paper, drainability of recycled fibres, hornification of the fibres and stickies contamination.

The main problem with recycled pulp is that due to high relative surface area of fines, dewatering rate is lower compared to virgin pulp. Thus, the productivity of the paper making process is considerably decreased compared to operation using virgin pulp. When cellulolytic enzymes are used for partial hydrolysis of cellulose chains to form a better recycled fibre structure, it is important to find the balance between two opposite directions. On one hand, by the hydrolysis of fines improved dewatering rate is obtained. On the other hand, enough fines have to be left in the pulp in order to obtain optimal inter fibre bonding, which is required for good strength properties of the end product. Moreover, enzyme action should not result in excessive hydrolysis, as this means loss of weight and thus production.

Recycled fibres can be upgraded through enzymatic treatments with cellulases. In fact, the enzymes modify the interfacial properties of fibres, increasing the water affinity, which in turn change the technical properties of pulp and paper, such as

drainability and strength (Pala et al., 2002). Relative bonded area (RBA), flexibility and fibrillation can be modified with endoglucanase in order to improve fibre properties. Such an effect can increase the rate of production on drainage- limited paper machines. Studies have shown that a judicious choice of the enzyme component, its dosage and the duration of treatment can make it possible to achieve significant freeness increase, while still not causing unacceptable levels of degradation to the fibres (Bhat et al.1991; Eriksson et al.1998).

Jackson et al. (1993) suggested that enzymes can either flocculate or hydrolyze fines and remove fibrils from the surface of large fines. The enzyme aided flocculation occurs when a low enzyme dosage is used. In this case, fines and small fibre particles aggregate with each other or with the larger fibres, decreasing the amount of small particles in pulp and consequently improving pulp drainage. For higher enzyme concentration, flocculation becomes less significant, and hydrolysis/fragmentation of fines begins to predominate.

The following research work investigates the impact of four different cellulase based preparations on the drainage of recycled pulp and paper strength.

Material & Methods

Recycled Pulp Furnish

The recycled pulp furnish with coated book stock, sorted office pack, old record in 20:40:40 ratio was collected from a paper mill.

1. Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur -247001 (U.P.)

2. Thapar Centre for Industrial Research and Development, Paper Mill Campus, Yamuna Nagar -135001 (Haryana)

Cellulase Enzyme Blends

Different commercial enzymes from different enzyme manufacturers were used. These included enzyme mix of various cellulase components, monocomponent endoglucanase & cellobiohydrolase preparations. The enzyme preparations were characterized by their activity against standard substrates. Enzymes A & B contained a multi component preparation containing a natural blend of enzymes having more cellobiohydrolase activity. Enzyme C was a mix blend of enzymes containing both endoglucanase and cellobiohydrolase enzymes components in sufficient quantity. Enzyme D was an engineered blend of mainly endoglucanases with side activities of cellobiohydrolase.

Characterization of enzyme preparations

The endoglucanase activity of enzyme preparations was determined using sodium carboxy methyl cellulose (CMC) as a substrate (Ghose 1987). The reducing sugars were determined by dinitrosalicylic acid procedure (Miller, 1959), with glucose as a standard. The activity was expressed in IU/ml.

The exocellulase (cellobiohydrolase, CBH) was determined with p-nitrophenyl- β -D-glucoside (pNPG) (Sigma, USA) as a substrate (Gusakov 2005). Quantity of p-nitrophenol released was determined using its extinction coefficient ($18,300 \text{ M}^{-1} \text{ cm}^{-1}$) and then the enzyme activity was calculated.

The FPase activity was determined by incubating 0.5 ml of suitably diluted enzyme with 50 mg of Whatman No. 1 filter paper of 1 cm *6 cm size (Ghose 1987). After 60 minutes of incubation at 50 °C the reducing sugars were measured in the supernatant by dinitrosalicylic acid procedure (Miller, 1959), with glucose as a standard. The activity was expressed in FPU/ml.

Enzyme Treatments

The recycled pulp was disintegrated in a sheet disintegrator for 2000 revolutions to disperse the fibers. All enzyme treatments were done at 4% consistency, 45°C and pH ~ 7. The enzyme based products were added at varying dosage of 100 to 250 gm product per O.D. tonne pulp. The enzyme products were mixed/incubated with the pulp slurry for 30 minutes prior to filtering the slurry through a Buchner funnel using a Whatman no.1 filter paper. The control sample was treated in the same manner as the enzyme treated samples with the exception of enzyme addition.

Drainability of pulp

The drainage time of the pulp slurry was measured on modified °SR tester using the method used by previous researchers (Litchfield, 1994 & Bhardwaj et.al., 1995 &1997, Hubbe, 2003). The equivalent amount of 2 g (oven dry) pulp from the pulp slurry was taken and made-up to 1 L using cold filtered water to maintain the final temperature of pulp stock at around 20 °C. The back (vertical) orifice of the tester was closed using a rubber stopper and the pulp slurry was taken in the jar of the tester. The time required to drain the water from pulp slurry for collection of 800 mL filtrate from the

front orifice was measured and reported as the drainage time in seconds.

Hand sheet Preparation and Testing

The hand sheets were prepared immediately following enzyme treatment to avoid extended contact time with the cellulase enzymes. The treated and filtered pulp was diluted to a consistency of 0.3% and hand sheets were prepared according to TAPPI test method T 205 sp-06. The standard hand sheets were conditioned at 27°C and 65% relative humidity. The strength properties were tested according to TAPPI test methods.

Results

Activities of enzyme samples

Different activities of the enzyme samples were evaluated by the respective methods given in the materials and methods section. CMCase, Cellobiohydrolase & FPase activities were evaluated at pH 6.0, 7.0 & 8.0 at temperature 50 °C and are shown in Figure 1.

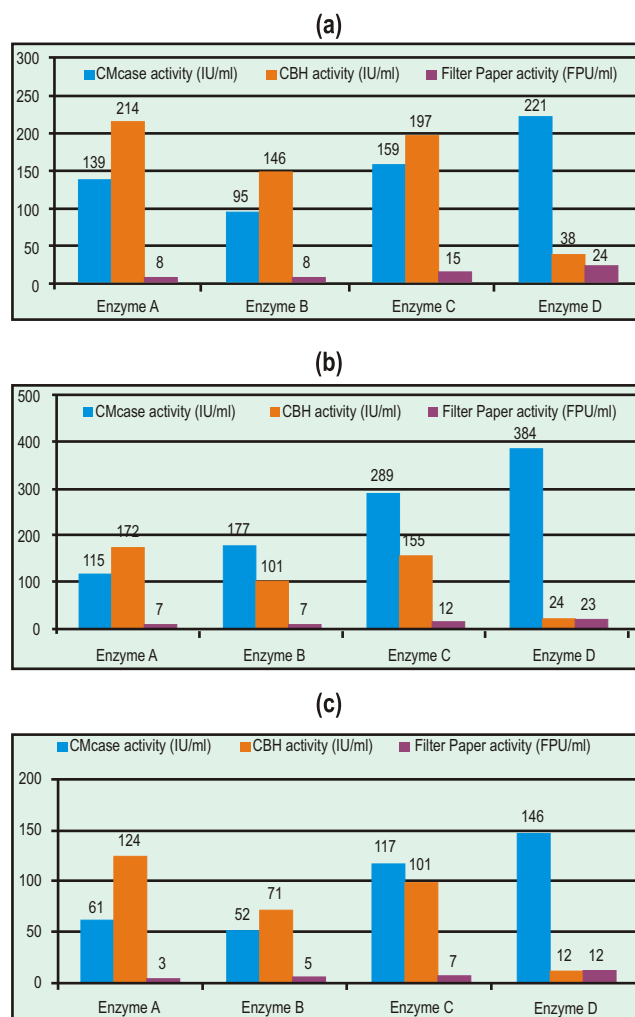


Figure 1: Various enzyme activities (CMCase, Cellobiohydrolase, FPase) of different enzymes at temperature 50 °C at pH (a) 6.0 (b) 7.0 (c) 8.0

Enzyme D has the highest CMCase activity i.e. endoglucanase activity as compared to other enzymes. Enzyme A was found to exhibit higher cellobiohydrolase activity when compared with other enzymes.

Effect of Enzyme treatments on drainability of pulp

Enzyme D having the highest endoglucanase (CMCase) activity displayed the highest improvement in pulp drainage (ranging from 11.5 to 25.1%) in comparison to other enzymes at various dosages in recycled pulp.

Enzyme A having the highest cellobiohydrolase activity but lowest endoglucanase activity was not found suitable in improving the recycled pulp drainage.

Enzyme C having both high endoglucanase activity (CMCase) as well as high cellobiohydrolase activity was also found effective in improving the pulp drainage ranging from 9.5 to 17.2% at various dosages in different recycled mill pulps (Table 1, Figure2). The strength properties were reduced for enzyme C treated pulps.

After studying the effects of different enzymes having different activities, we can say that the presence of endoglucanase activity is a prerequisite for improvements of drainage of recovered paper by enzymatic means. Endoglucanases enhance dewatering by hydrolyzing the amorphous hydrophilic cellulose which is the main constituent of the fines.

Effect of Enzyme treatments on pulp viscosity

Analysis of pulp viscosity was based on TAPPI standard test method T230 om-99. The pulp viscosity was somewhat reduced in all enzyme treated pulp samples. But, the reduction in pulp viscosity was more prominent in enzyme C treated samples, whereas the enzyme A & enzyme D treated samples displayed a slight decrease in viscosity (Table 1, Figure 3).The reason may be high amount of enzyme components i.e. endoglucanase & cellobiohydrolase in enzyme C.

Effect of enzyme treatments on paper properties

The effect of enzyme D treatment on the pulp strength properties showed significant increase in breaking length, while the tear factor was decreased. The reason for increase in breaking length may be due to increased fibrillation and inter fibre bonding. The reduction in tear strength in Enzyme D treated recycled pulp was somewhat lower if compared to other enzyme treated pulps. Improvement in smoothness of enzyme treated pulps was also observed. Probably the enzyme D action contributes to an improvement of paper structure independent of fibre degradation processes (Table 1, Figures 4, 5).

Conclusion

Significant improvement in drainage, about 11 to 25%, was observed using enzyme D (endoglucanase) treated recycled pulps at different enzyme dose. Breaking length was improved by 16%. However, at high dose (250 g/tp) of enzyme, reduction in pulp

Table 3: Effect of enzyme dose (different enzymes, dosage) on drainability, pulp viscosity & strength properties of recycled mill pulp

Particular	Blank	Enzyme A					Enzyme B					Enzyme C					Enzyme D				
		100	150	200	250	300	100	150	200	250	300	100	150	200	250	300	100	150	200	250	300
Enzyme Dose (g/t)	--	100	150	200	250	300	100	150	200	250	300	100	150	200	250	300	100	150	200	250	300
CSF (ml)	350	350	360	365	370	375	360	365	370	375	380	365	370	375	380	385	370	375	380	385	390
Change in CSF(ml)	--	--	+10	+15	+20	+25	+10	+15	+20	+25	+30	+15	+20	+25	+30	+35	+20	+25	+30	+35	+40
Drainage time for 800 ml (sec)	41.01	41.2	39.6	39.3	37.8	36.2	41.2	40.2	39.1	36.7	35.1	37.5	37.2	36.1	34.8	33.5	37.0	36.1	34.7	32.3	30.8
Decrease in Drainage time %	--	0	3.4	4.3	8.1	12.2	0	2.0	4.7	11.0	14.5	9.5	10.1	13.2	17.2	21.5	11.5	13.2	17.4	25.1	32.3
Viscosity, cP	4.8	4.9	4.9	4.7	4.4	4.1	4.4	4.3	4.2	4.0	3.7	4.4	4.2	4.2	4.0	3.7	4.8	4.6	4.5	4.5	4.5
Effect on physical strength properties																					
Grammage (g/m ²)	71.2	71.6	71.4	71.0	70.7	70.3	71.3	70.9	72.5	70.6	71.1	71.2	72.6	71.2	72.1	72.6	72.1	70.8	72.6	71.4	71.4
Bulk (cc/g)	1.53	1.54	1.52	1.53	1.52	1.51	1.53	1.52	1.52	1.53	1.53	1.51	1.52	1.53	1.54	1.53	1.54	1.54	1.52	1.52	1.52
Breaking length(m)	2248	2278	2281	2209	2321	2351	2251	2312	2132	2281	2281	2376	2408	2474	2349	2407	2349	2407	2498	2617	2617
Tear factor	66.3	67.5	67.4	66.3	67.8	68.4	63.4	61.7	60.3	58.4	64.1	63.9	62.6	61.7	64.7	63.3	64.7	63.3	62.8	62.6	62.6
Burst Factor	15.3	15.3	15.2	15.3	15.2	15.3	15.3	15.2	15.2	15.2	15.1	15.1	15.3	15.3	15.3	15.1	15.3	15.1	15.3	15.2	15.2
Double fold (nos.)	8	7	14	9	16	16	9	14	10	19	10	19	9	24	9	15	9	15	12	27	27
Bendsten Roughness, mL/minute	204	202	191	208	196	178	178	165	161	151	167	151	143	132	165	150	165	150	137	112	112

Enzyme treatment conditions: time 30 min, temp. 45 °C, pH 7.0±0.5

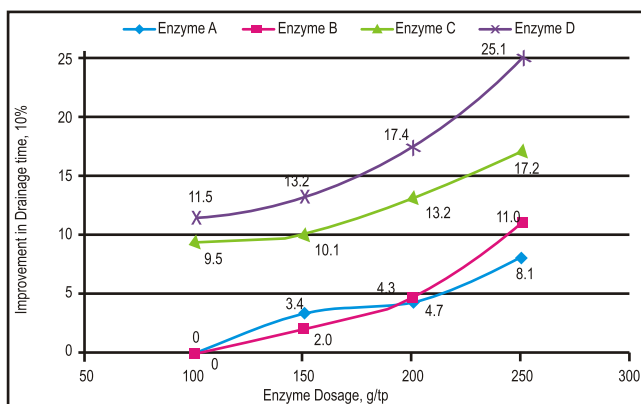


Figure 2: Effect of enzyme dose on drainage time of treated pulps

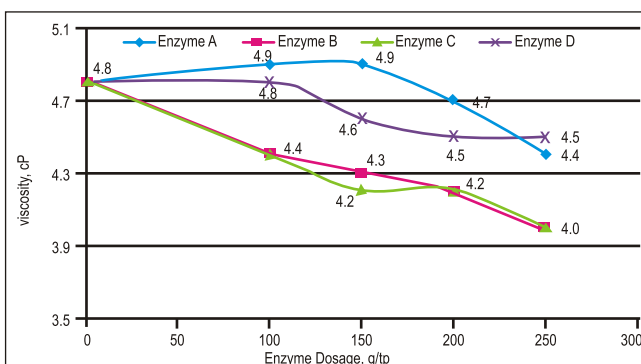


Figure 3: Effect of enzyme dose on pulp viscosity of treated & untreated pulps

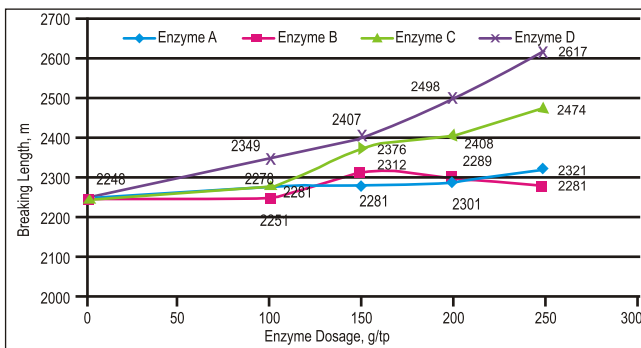


Figure 4: Effect of enzyme dose on breaking length of treated pulp

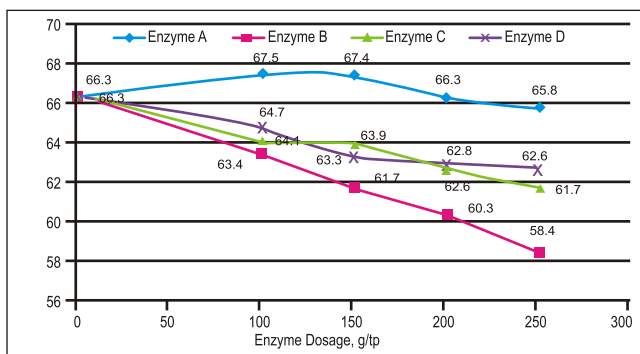


Figure 5: Effect of enzyme dose on tear factor of treated pulp

viscosity was observed with slight reduction in tear strength. Enzyme A and B were not found effective for improving the drainage of pulp significantly. Enzyme C improved the drainage of pulp, but the pulp viscosity reduced and tear strength got deteriorated. The results indicate that applying specific cellulose component, i.e. endoglucanase, may be more effective for improving the drainage of recycled pulp.

Reference

- Bhardwaj, N. K., Bajpai, P. and Bajpai, P. K. (1997), Enhancement of strength and drainage of secondary fibres. *Appita*: 50 (3) 230-232.
- Bhardwaj, N. K., Bajpai, P. and Bajpai, P. K. (1995), Use of enzymes to improve drainability of secondary fibres. *Appita*: 48 (5) 378-380.
- Bhat GR, Heitmann JA, Joyce TW (1991), Novel techniques for enhancing the strength of secondary fiber. *Tappi J.*; **74**(9) pp 1511-1517.
- Dienes, D., Egyházi, A., Réczey K. (2004), Treatment of recycled fiber with *Trichoderma* cellulases, *Industrial Crops and Products*, **20**, pp1121.
- Eriksson, L.A., Heitmann, J.A., Jr., and Venditti, R.A. (1998), Freeness improvement of recycled fibers using enzymes with refining, in *Enzyme Applications in Fiber Processing*, ACS Vol.X.
- Miller GL. (1959), Use of Dinitrosalicylic Acid Reagent for Determination of Reducing Sugar. *Anal. Chem.* 31: pp 426-428
- Ghose, T. K. (1987). Measurement of cellulase activities, *Pure and Applied Chemistry J.*, **59** (2), pp 257-268.
- Gusakov AV, Sinitsyn AP, Salanovich TN, Bukhtjarov FE, Markov AV, Ustinov BB, van Zeijl C, Punt P, Burlingame R. (2005) Purification, cloning and characterization of two forms of thermostable and highly active cellobiohydrolase I (Cel7A) produced by the industrial strain of *Chrysosporium lucknowense*. *Enzyme and Microbial Technology J*, 36:57-69.
- Hubbe, MA. (2003) Selecting laboratory tests to predict effectiveness of retention and drainage aid programmes, *Sci. & Tech. Advances in Fillers & Pigments for Papermakers*, Pira, Leatherhead, Surrey, UK, paper 4.
- Jackson LS, Heitmann JA, Joyce TW. (1993), Enzymatic modifications of secondary fiber. *Tappi J.*, **76**(3):pp147-154.
- Litchfield, E. (1994). "Dewatering aids for paper applications," *APPITA J* 47: 62-65.
- Oksanen T, Pere J, Paavilainen L, Buchert J, Viikari L. (2000), Treatment of recycled kraft pulps with *Trichoderma reesei* hemicellulases and cellulases. *J Biotechnol*; **78**: pp394-408.
- Stork G, Pereira H, Wood TM, Du'sterhoft EM, Toft A, Puls J. (1995) Upgrading recycled pulps using enzymatic treatment. *Tappi J*; **78**:pp798-808.