Implementation of Xylanase Prebleaching in Indian Paper Industry

R. K. Jain[1], R. M. Mathur[1], Vasanta V Thakur[1], Piyush Veerma[1] and A. G. Kulkarni[2]

Xylanase enzymes have been successfully employed in pulp & paper manufacturing to reduce chlorine based bleaching chemical demand. Introduced commercially, the process has been in use in several mills in North America, Europe and other parts of the world. However, the process has yet to be commercialized in an effective way in Indian paper industry on regular basis. The paper describes the efforts of CPPRI in implementation of enzyme prebleaching process in an Indian paper mills.

INTRODUCTION

Over the last decade, the active and potential applications of enzymes in the production of pulp and paper has steadily grown with several process being used on a commercial scale. It is generally accepted that enzymes have the potential to provide beneficial effect at all stages during pulp and paper manufacturing. These opportunities have not been fully realized due to certain limitations associated with enzyme technology. One of the limitations has been the poor correlation of the targeted process outcome with the appropriate enzymatic action and lack of suitable enzymes able to work with in the range of existed process conditions.

Pulp bleaching has been targeted as one of the potential application for enzymes in pulp and paper process. Central Pulp and Paper Research Institute (CPPRI) has carried out extensive studies in the recent past for promotion of environmentally compatible processes in Indian paper industry, the process and enzyamatic prebleaching of pulp is the one among these. As a part of one of the project, the Institute evaluated several xylanases enzymes (indigenously developed as well as commercially available) on wood and non-wood based pulps being employed in Indian paper industry. These studies were carried out at the Institute's Laboratory and at various pulp and paper mills in different part of the country.

During the study, it was observed that mixing, of enzyme with the pulp at medium consistency has been one of the factors limiting to achieve the desired efficiencies. Having carried out exhaustive studies, the same was taken care by fabrication and installation of the identified equipments in a large integrated paper mill, identified by Indian Paper Manufacturers Association (IPMA) to demonstrate the process for enzymatic prebleaching of pulp.

The objective of the trial was to identify the potential to reduce the applied charges of chlorine using identified xylanase enzyme on kraft pulp with simultaneous reduction in release of chloro organic compounds (AOX) without adversely effecting the quality of the pulp.

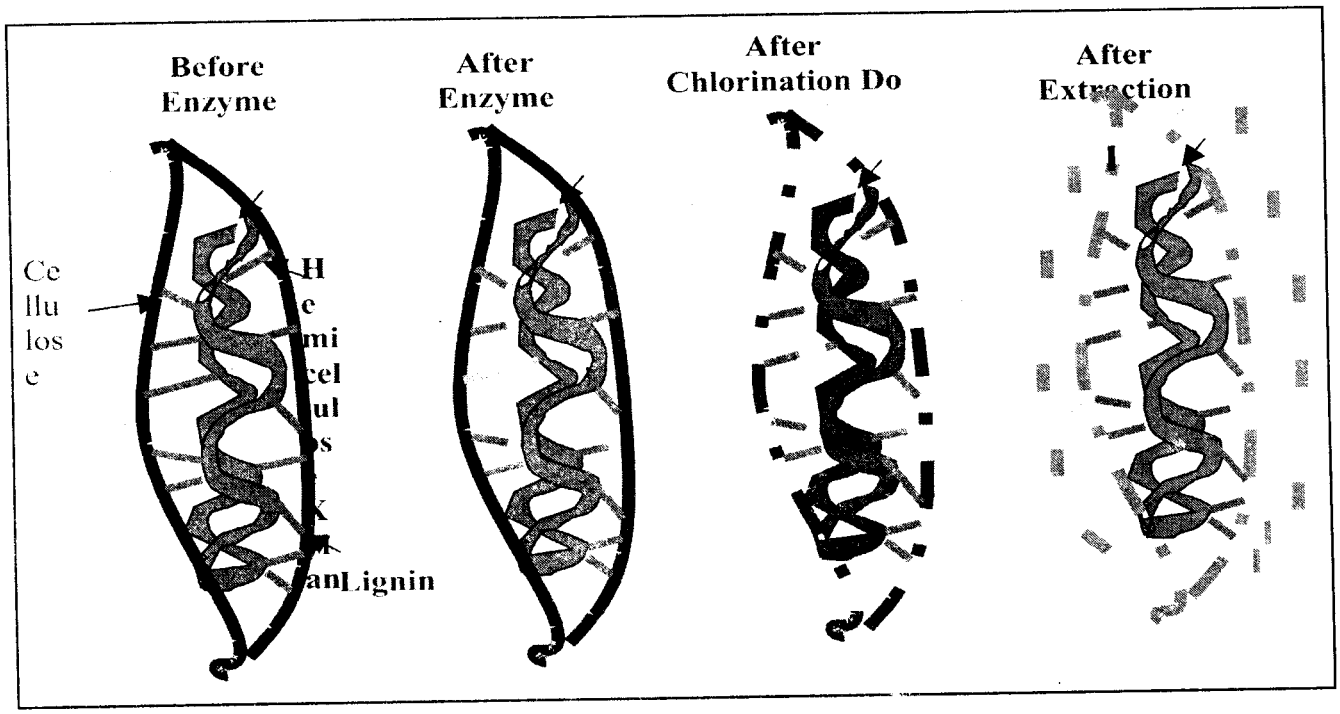
Novel Xylanase Enzyme as bleach booster

Xylanase is an enzyme that catalyzes the hydrolysis of 1,4-b-D-xylosidic linkages in xylan, a hemicellulose in pulp. Several industrial Xylanase preparations are commercially available, with many other natural xylanases having been identified. Variations in xylanases can occur between size, structure, amino acids, position attacked on the xylan, attachment to xylan, stability in the pulp slurry and also stability while acting on the pulp. Not all xylanase work with all pulp sources, indeed literature survey reveals that some of enzymes work with beter than others due to the synergy among xylanase or the carbohydrates. In general most of the xylanase used forbleaching belong to the family G (or 11) enzymes, which are smaller that those in family F(10). While all xylanases release xylose from natural xylan, the differences between commercial Xylanase preparations can significantly impact the bleach boosting effect.

Effective xylanases should preferentially have the characteristics like:

- These should be stable on kraft pulps. Some xylanase preparations non-specifically absorb to pulp fibers and are inactivated by degradation products from kraft pulping;
- These should have a neutral to alkaline pH optimum since residual

1 Scientists, 2 Director
Central Pulp & Paper Research Institute, P. O. Box No. 147, Saharanpur - 247001 (India)



alkali leaks out of the pulp during enzyme treatment, and the pH of even well washed pulp stocks can shift upwards dramatically.

- These should have good thermal stability.

How Xylanases Act and Improves Bleachability?

Xylanases such as endoxylanases are xylan-specific enzymes. They catalyze the hydrolysis of xylose-xylose bonds within the xylan chain and only solubilize a fraction of the total xylan present. Xylanase treatment can improve lignin extraction, alter carbohydrates and lignin association or cleave reabsorbed xylan.

One possible mechanism is that xylan reabsorbed on the fiber surface during kraft pulping and creates a barrier against lignin removal during bleaching with bleach chemicals. The xylanase treatment may remove the xylan barrier allowing better access by bleaching chemicals to residual lignin covered up by the xylan barrier.

The other possible mechanism suggest that readsorbed xylan may be chemically bonded to residual lignin in pulp. These lignin carbohydrate complexes (LCC's) are thought to be difficult to be removed due to diffusion limitations. According to this hypothesis, by cleaving xylan chains involved in these complexes, smaller residual structures of increased mobility are formed. The increased mobility allows for easier removal of these structures from the fiber.

Xylanase enzyme cleave the xylan that allow the removed of such groups. This may result in savings as chemicals that would be needed to bleach these residue. The removal of the hexenuronic acid by xylanase treatment also help in respect of brightness reversion of the treated kraft pulp.

It has also been suggested that one UV absorbing material, hexenuronic acid is formed during kraft pulping from methylglucuronic acid residues present on xylan. The cleavage of the xylan allows the removal of such groups,

Fig. 1 Medium Consistency

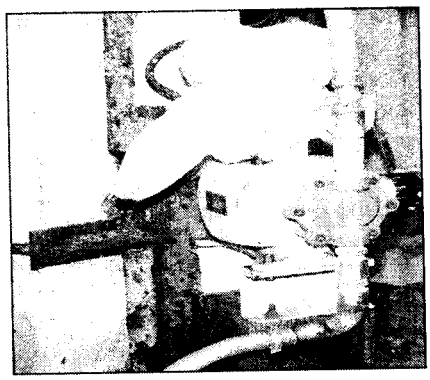


Fig. 2 Dosing Pump

Fig. 3 Stand Pipe

resulting in savings of bleach chemicals, that would be neded to bleach those residues.

Mill Description and Trial Preparation

The identified mill for enzymatic prebleaching trial was an integrated pulp and paper mill employing eucalyptus, casuarinas and bagasse as major fibrous raw material producing nearly 300 tpd of bleached variety of paper. The hard wood pulp is cooked to a kappa no. of 22-24. Brown stock pulp is washed through vacuum washers and screened prior to thickness in high density storage and bleaching. The bleach sequence used was CEp1Ep2H.

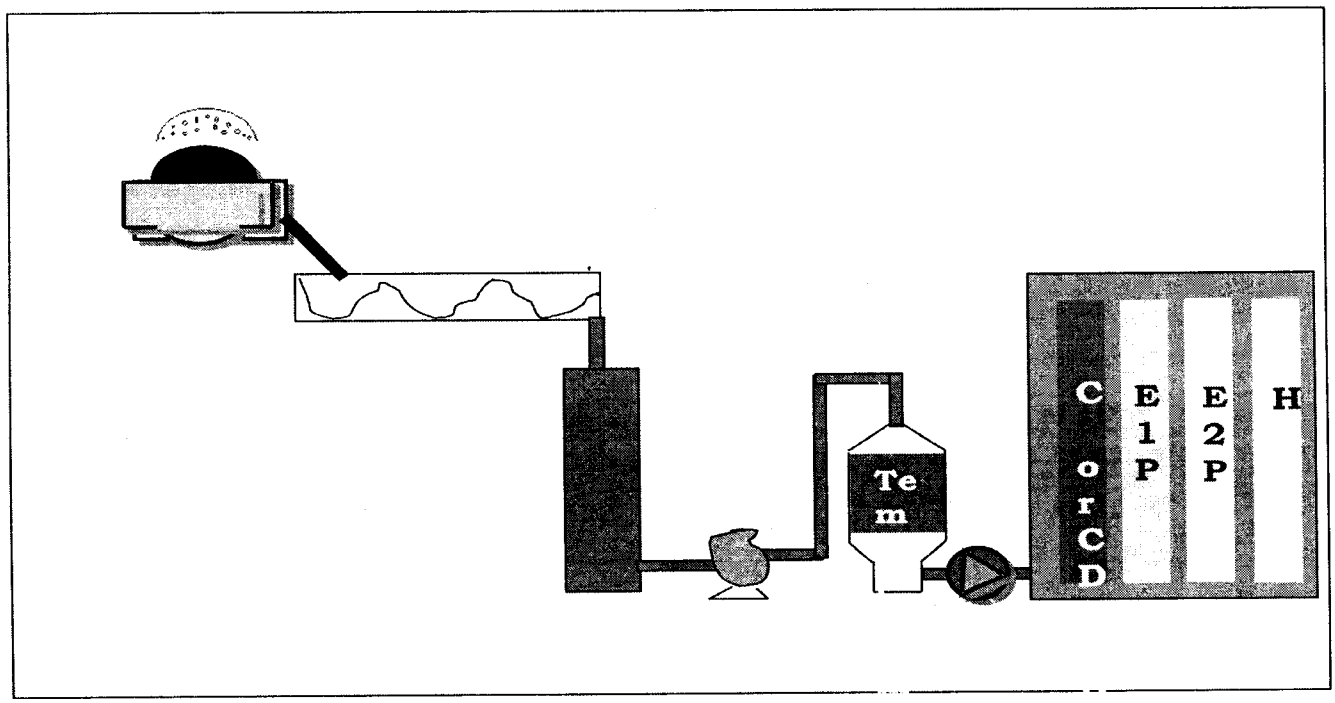
After commissioning of the additional required equipments like MC Pump, Stand Pipe, Enzyme Dosing Pump (Fig. 1,2 & 3), a sparger at the pulp conveyer, the mill trials were continued over a period of two weeks in June, 2005.

Table 1

Results of Xylanase Enzyme Treatment of Pulp – Optimization studies at the mill

Unbleached Unscreened Pulp-pH 9.9; Temp. 0C-65; Kappa – 23.6; Brightness, %-29; Soda loss, kg/tp-14-15

Particulars	Control	Enzyme treated pulp		
	1	2	3	4
Enzyme dose, kg/tp	-	0.50	0.65	0.75
Temp, °C	60	60	60	60
PH	9.6	9.6	9.6	9.6
RT, hrs	1.5	1.5	1.5	1.5
Consistency,%	8.0	8.0	8.0	8.0
After Enzyme Treatment-Pulp				
Kappa No.	19.6	18.5	18.5	17.0
Brightness,%	31	32	32	32
After Enzyme Treatment – Pulp Extract				
Colour, kg/tp	70	101	-	104
Bleached sequence - CE(p)E(p)H				
Chlorination stage				
Appl. Cl_2 Dose, %	4.53	4.53	3.85	3.7
Consumption,%	82	84	84	84
Cl_2 Savings, %	-	-	15	18
P. No.	7.3	7.6	7.7	7.5
Brightness, %	47	48	48	47
E(P) 1 Stage				
Applied NaOH,%	1.0	1.0	1.0	1.0
Applied H_2O_2, %	0.75	0.75	0.75	0.75
Residual H_2O_2, %	0.02	0.02	0.02	0.04
P. No.	7.0	6.9	7.0	7.2
Brightness, %	62	63	62	62
E(P) 2 Stage				
Applied NaOH,%	1.25	1.25	1.25	1.25
Applied H_2O_2, %	0.75	0.75	0.75	0.75
Residual H_2O_2, %	0.05	0.03	0.04	0.03
P. No.	6.0	6.8	6.8	6.6
Brightness, %	62	63	62	62
Hypo stage				
Applied Hypo,%	1.6	1.6	1.6	1.3 1.6
Consumption,%	82	80	72	78 80
Applied NaOH,%	0.25	0.25	0.25 0.25	0.25
Hypo savings,%	-	-	- 19%	-
Brightness, %	83	84	83	83 83



Process Flow Sheet of Enzyme Prebleaching Trials at SPB Ltd., Erode

Equipment for Enzyme Prebleaching

Before starting the trial the existing mill data and samples of the pulp and effluents for various stages were collected to take as control reference and evaluated for parameters of interest.

The consignment sample of the Xylanase enzymes, identified by CPPRI was evaluated at the mill in order to optimize the enzyme doses under existed pulp mill conditions. After evaluation of the sample, the optimum dose of the enzyme in both the cases were found to be around 0.65 kg/tp with potential for saving of chlorine at "C" stage and hypo stage to a targeted level i.e. around 15% while maintaining the targeted brightness level of +82% ISO in the bleached pulp. Results are shown in Table-1.

RESULTS & DISCUSSION

After ensuring the stabilized conditions in the pulp mill, enzyme dosing was started from 14th November 2005 onwards at optimum dose of 0.65 kg/tp and continued over a period of more than a week. The effect of enzyme treatment started reflecting within 24 hrs both with

Table 2

Results of treatment of xylanase in respect of unbleached and bleached pulp during mill trials

Date	Screened pulp		Cl2 Stage		Extraction-1		Extraction-2		Hypo-Stage	
Bleached pulp										
	Kappa No.		Kg/tp/Applied%		Brightness	Kappa No.	Brightness %		Kappa No.	
Brightness %		Appl, %	Brightness, %		PC No.					
14.11	22-24		36	5.6	43	3.6	54		82-83	2.5
15.11	22-24	5.04	38	5	43	3.6	54	58.8	82-83	2.2
16.11	22-24		36	5.3	43	3.8	54		82-83	2.5
17.11	21-22		41	*	50	3.5	60		83	1.7
18.11	21-22		41	*	44	*	49		82-83	1.7
Enzyme dosing 750 gm/tp										
19.11	22-24		38	*	42	*	53		82-83	1.7
20.11	21.3		40+	5.2	43+	3.4	55+		82-83	1.7
21.11	21		41-43	4-5.2	45-52	3-3.3	55+	50.8	82-83	1.7
22.11	21	4.04%	38-45	4-4.9	42-46	3.0-3.5	55-59		82-83	1.7

Table 3

Strength Properties of bleached and unbleached pulp before and after enzyme treatment.

Particulars	Without Enzyme 14.11.05 to 18.11.05	With Enzyme 19.11.05 – 24.11.05
Strength properties – Unbleached pulp		
Bulk	1.36-1.40	1.38-1.41
Burst Index, kPa.m²/g	5.6	5.6
Tensile Index, N.m/g	87-90	89.2
Tear Index, mN.m²/g	6.8	7.1
Strength properties – Hypo bleached pulp		
Burst Index, kPa.m²/g	4.5-4.6	4.6-4.7
Tensile Index, N.m/g	70-74	74-75
Tear Index, mN.m²/g	4.9	4.9
Brightness, % ISO	83	83
P.C. No.	2.5	1.7

unbleached and bleached pulps.

Effect of Xylanase Enzyme on Kappa No. & brightness of enzyme dosing of the Pulps

Treatment of the pulp with xylanase enzyme, resulted in reduction in kappa of unbleached pulp which was dropped from an average of 23.0-25.0 to 21.0-22.0 as shown in Figure-5, Table-2. There was also drop in the kappa number at the subsequent stages during bleaching i.e. at Chlorination stage it was dropped from 7.0 to 6.0, at EP1 stage drop in kappa no. was from 5.0 to 4.0 and at EP2 stage. This was from 4.0 to 3.0 with gain in brightness of the pulps around 2-3 units at each stage respectively as shown in Table-2, Fig.-6.

Effect of Xylanase treatment on requirement of chlorine charge

Having observed the positive indications of the enzyme treatment which reflected as drop in Kappa No. of unbleached pulp and also as increased in level of residual chlorine in filtrate from 'C' stage (from 50 ppm to more than 250 ppm) and at 'H' stage (from 400 ppm to more than 1000 ppm) (Fig-7 & 8), it was decided to reduce initially the chlorine charge at C stage. The charge could be reduced from average required dose of 5 kg/tp to 4.0 kg/tp. After decreasing the dose of elemental chlorine at 'C' stage, it was observed that there is a scope for reducing the chlorine charge at hypo while maintaining the target brightness level of 82 – 83%. Accordingly the hypo flow was reduced from an average rate of 16.8 m³/hr (84%) to 15.0 m³/hr (75%) and targeted brightness 82-83% ISO could be achieved.

From the results shown in Table-2, it is observed that around 15% savings of the total chlorine both during "C" stage and "H" stage could be possible. The studies further indicated that there is potential for saving of more chlorine after overcoming the certain process limitations.

Effect of Xylanase treatment on strength and optical properties of the pulp

Based on trials, the results of strength and optical properties of unbleached and bleached pulp before and after enzyme treatment are shown in Table-3. From the results it was observed that no drop in strength properties was observed, however, there was slight improvement in the strength properties of bleached pulp. In case of bleached pulp the burst index improved from values of 4.5 – 4.6 to 4.6-4.7 Kpa.m²/g, tensile index 74-75 from 70-74 Nm/g without loss in tear index which could be maintained at 4-9 MN.m²/g. One of the important advantages of xylanase enzyme treatment was in respect of optical properties particularly the post color number (PC No.) which was reduced significantly. The P.C No. was reduced from value of 2.5 to 1.7 indicating nearly 40% reduction.

Environmental effect of enzyme treatment

Table-4 show the results of pollution loads in terms of AOX and COD in composite bleach effluent.

Reduction in requirement of chlorine

Table 4

Particulars	Without Enzyme Enzyme	With Enzyme 17.6.05-26.6.05
	Combined	
AOX, ppm/kg/tp	46.5	35.3
Reduction in AOX, %	-	22%
COD, ppm	700-820	672-800

Photograph during mill trial on Enzymatic Prebleaching of Pulp at Seshasayee Paper & Board Ltd., Erode

of around 15% resulted in lowering the AOX level in bleach effluent which were reduced to a level of around 22%.

Possible Benefits of Xylanase Prebleaching of Kraft Pulps

1. Brightness Gain : Xylanases improve bleaching chemical efficiency, leading to higher pulp brightness. This benefit is particularly attractive for mills with shortened bleaching sequences needing a high final brightness.

2. Chemical Savings: If the xylanases increase brightness in the bleach plant, the mill can cut chemical use and still attain the original target. Saving money with lower chemical use is the primary driving force for mills to adopt enzymes.

3. AOX reduction : Using enzymes to reduce chlorine charge can also reduce AOX in the combine mills' effluent.

4. ClO_2 Limitation : The ability to generate an adequate supply of chlorine dioxide may be a bottleneck. Enzymes can effectively make more ClO2 available since less is used per ton, leading to increased production.

5. Other benefits : Two Scandinavian mills are using enzymes to eliminate the D0 stage completely, while maintaining brightness targets. This has allowed the mills to send bleach filtrates prior to D stages back to recovery and resulted in partial closure of their water loop.

CONCLUSION

1. Enzymatic prebleaching of chemical pulps using xylanase enzyme could prove to be an effective technology in reducing the chlorine demand by 15% which maintaining – targeted brightness leve of +82% ISO.
2. Before introducing enzyme prebleaching technology in any mill it is important to evaluate a particular enzyme preparation for its response towards pulp for various parameters like temp., pH, enzyme activity and cellulose contamination.
3. Installation of Enzyme mixing device for proper mixing of enzyme with the pulp has proved to highly effective and helped in achieving the desired results.
4. AOX level in bleach effluent could be reduced to a level of at least 25% in case of kraft pulps with from wood and non-wood based raw materials employed in Indian paper industry.
5. The technology needs to be boosted in Indian paper industry in order to explore the possibilities of achieving desired standard norms, in respect of the AOX levels.

REFERENCES

1. Wong. K.K.Y; Martin. L.A; Garna F.M; Saddler. J.N & De Jong. E; "Bleaching boosting and direct brightness by multiple xylanase treatments during peroxide leaching of Kraft pulps"; Biotechnology Bioengineering; 54:312-318(1997).
2. Jain R. K,. Mathur R.M & Kulkarni. A.G; "Enzymatic prebleaching of pulps: challenges & opportunities in Indian pulp & paper industry"; 8th International Conference on Biotechnology in the Pulp & Paper Industry 8th (ICBPPI), held at Helsinki, Finland; June 4 -8, (2001).
3. Kirk T. Kent and Jeffries W. Thomas; "Roles for Microbial Enzymes in Pulp and Paper Processing", Chapter-1, page 1-12.
4. Kantelinen. A; et.al. "Proposed mechanism of the enzymatic bleaching of Kraft pulp with xylanases"; Holzforschung; 47: 318-324(1993).
5. Wong. K.K.Y. De Jong. E, Saddler. J.N & Allison. R.W; "Mechanism ofxylanase aided bleaching of Kraft pulp. Part-II Target substrates"; APPITA J. 50: 509-518(1997).
6. Viikari, Liisa, Suurnakki, A. and Buchert, J. "Enzyme Aided bleaching of Kraft Pulp : Fundamental Mechanism and Practical Applications", ACS Symposium Series, 655, American Chemical Society Washington DC. P.18-19, 1996.
7. Viikari, L., Suurnakki, A., and Buchert, J., "In Enzymes for Pulp and Paper Processing", Jeffries, T. W., and Viikari, L. Eds., ACS Sym. Ser. 655, American Chemical Society: Washington, 1996, p.15, 1996.
8. Claude, Daneault., Celine, Leduc., and Jacques, L, Valade. The use of Xylanases in Kraft Pulp Bleaching: a Review. Vol. 77, No. 6, Tappi Journal, 1994.
9. Jean, P., Hamilton, J., and Senior, D.J. Mill Trial Experiences with Xylanase: AOX and Chemical Reductions. Pulp & Paper Canada 95:12 (1994).
10. Bailey, M.J. Bailey, P & Poutanen. K; "Interlaboratory testing methods for assay of xylanase activity", J. Biotechnology; 23: 257-270, 1992.
11. Davis, M.; Rosin, B.; Landucci, L.L.; Jeffries, T.W. Tappi Biological Symposium, Tappi Press, Atlanta, San Francisco, 435-442, 1997.
12. Jiang, Z.-H., Van Lierop, B.; Berry, R. Tappi J., 83, 167-175, 2000.
13. Laine, J., Buchert, J., Viikari, L., Stenius, P., Holzforschung, 50, 208-214, 1996.
14. Suurnakki, A., Heijnesson, A.; Buchert, J.; Westermark, U.; Viikari, L.J. Pulp Pap. Sci., 22,J91-J96, 1996.
15. Chakar, F.S., Allison. L., Rangauskas, A.J. Mcdonough, T.J. Sezgi U.O. Tappi J., 83,62, 2000.
16. Buchert, J., Bergnor, E., Lindblad, G. Viikarhi L, Ek, M. Tappi J., 80, 165-171, 1997.
17. Suurnakki, A., Li, T-Q., Buchert, J., Tenkanen, M., Viikari, L. Vuorinen., T., Odberg, L. Holzforschug, 51,27-33, 1997.
18. De Jong, E., Wong, K.K.Y.; Saddler, J.N. Holzforchung, 51, 19-26, 1997.