Role of biotechnology in the pulp and paper industry : A Review

Part 2 : Biobleaching.

*Singh S.P. and Roymoulik S.K.

ABSTRACT

This is the second part of a three part review of role of biotechnology in the pulp and paper industry. Chlorine chemicals are needed to bleach conventional kraft pulp to full brightness, however, hazardous chlorinated derivates are formed. It has been shown that orgnanically bound chlorine or AOX formation mainly depends on the quantity of molecular chlorine used in the bleaching process. The pretreatment of kraft pulp with fungi and enzymes can replace the chlorine stage and consequently raduce the pollution load.

In part I of this series, biotechnology was defined as the use of biological organisms in biopulping[1]. Hence, we continue with a review of biotechnology research in biobleaching.

The main objectives of bleaching are to increase the brightness of the pulp and to make it suitable for the manufacture of printing and tissue grade papers by removal or modification of some of the constituents of the unbleached pulp, including the lignin and its degradation products, resins, metalions, non-cellullosic carbohydrate components and flecks of various kinds.

The residual lignin of unbleached kraft pulp is removed in a multistage bleaching procedure using a combination of chlorination and alkaline extraction stages in modern mills. The effluent from such bleaching process is a growing environmental concern due to its content of numerous chlorinated organic substances, including mutagenic chlorinated phenols and dioxins. There is a great interest, therefore, in eliminating, or atleast reducing the use of chlorine-based chemicals in bleaching.

White-rot fungi are the most attractive micro-organisms for the removal of residual lignin from kraft pulp by biological means. Kraft pulp delignification was first reported by Kirk and Yang[2] in 1979. Phanerochaete chrysosporium and other fungi lowered the kappa number of unbleached softwood kraft pulp by upto 75% when incubated for several days in shallow stationary layers and then extracted with alkali. A similar effect was observed with hardwood kraft pulp[3]. More recently, it was observed that the treatment of hardwood kraft pulp with coriolus versicolor resulted in an increase in pulp brightness with a corresponding decrease in residual lignin concentration [4, 5]. Tran and chambers[6] were able to remove 33.5% of lignin content in 10 days treatment with P. chrysosporium without any alkali extraction. Kappa number of Kraft pulp has been shown to decrease from 33 to less than 10 in two weeks treatment with chrysosporium in liquid culture[7].

Paice etal[8] studied the effect of nine fungal strains on hardwood kraftpulp under aerobic, agitated conditions. Coriolus versicolor resulted in an increase in pulp brightness with a corresponding decrease in resi-

Birla Research Institute
For Applied Sciences
Birlagram - 456 331 Nagda (M.P.) India

dual lignin concentration. The handsheet strength properties were imroved in treated pulp, inspite of viscosity drop indicating some cellulose chain cleavage. Combined fungal and chemical (DED) bleaching gave a pulp of 82% brightness, where as a conventional CEDED bleaching gave 88%. The results are given in table 1.

Fujta[9] etal reported that when the kraft pulp of hardwood was treated by coriolus versicolor, P. chrysosporium and coriolus hirsutus, reduce chemical dosage by 72% (based on effective chlorine), compared to the conventional bleaching process (CEDED), although a reduction of the kappa number of the pulp by the fungal treatment was 60%. Similar results was also obtained for softwood unbleached pulp i. e. bio-bleaching process (FCED) could reduce the chemical dosage by 73% and kappa number by 63%, compared to the conventional bleaching process CEDED. The results are tabulated in table 2. The white rot fungus trametes versicolor can delignify unbleached softwood kraft pulp and decrease its bleachability in agitated cultures. The pulp viscosity and zero span breaking length decreased due to the cellulose depolymerization. Sheet strength properties except tear were enhanced and pulp yield was high[10].

The slow pace of the fungal systems presents the same obstacle for bleaching as it does for pulping. So, the enzymes have been looked at as well. Enzymes are complex organic compounds secreted by living cells and are capable of causing or accelerating some change in an organic substance for which the enzyme is often specific. Enzymes are essential factors in natural and domestic functions ranging from the human digestive tract to soap powder for washing machine. Industrial enzymes are made from simple organic substances, such as glucose, by the action of carefully selected and genetically engineered organisms. Enzymes are not living organisms, and can be thought of as chemical catalysts.

The mill-scale trials and commercial operations are all based on adding some commercial variation of xylanase and acid to the brown stock. Xylanase enzymes have been widely reported to improve the effectiveness of conventional bleaching chemicals in removing lignin from hardwood and softwood kraftpulp. Xylanase enzymes acts to enhance bleaching by a different mechanism than does oxygen, chlorine, chlorinedioxide and other chemical methods. Lignin is chemically bound to carbohydrates, might have its removal facilitated by xylanase's novel attack on mechanism[11,12]. Xylanase enzyme[13] used in a simple treatment of unbleached pulp, has the same delignification and brightning capability as 5 to 7 Kg/t of Clo_2. The enzyme can be used to decrease the active Cl_2 used for the first stage of bleaching by 20% or decrease ClO_2 used in brightening by 5 Kg/t.

Perrolaz etal[14] treated brich kraft pulp with a thermostable xylanase in an elemental chlorine free bleaching sequence. After the enzymatic stages, the pulps were bleached by using $E_{p1}D_1E_{p2}D_2$ bleaching sequence and compared with two standard bleaching sequences, $CE_{p1}DIE_{p2}D_2$ and $(D_{50}C_5)$ $E_{p1}D_1E_{p2}D_2$ The results are plotted in table 3 the results showed that the consumption of active chlorine was reduced 6 to 15% when compared respectively to the reference sequence DC $EP_1D_1EP_2D_2$ and $CE_{p1}D_1D_{p2}$ D_2. Enzyme treated pulp and the chemical reference pulp have similar viscosity.

In pulping, undegraded and degraded xylans are dissolved in the cooking liqour to a considerable extent but as the cook proceeds, the Alkali concentration decreases below the critical point and degraded short chain xylan precipitates in a more or less crystalline form on the surface of cellulosic microfibrils[15]. The reprecipitated or readsorbed alkali-resistant xylan appears to form a physical barrier for the extraction of residual lignin from the fibres. Hence, the pretreatment of kraft pulp with hemicellulase enhanced extractability of lignin and consequently redce the consumption of bleaching chemicals[16].

Viikari and coworkers[17] used endoxylanase and B-xylosidases hemicellulase system produced by three organisms - Aspergillus awamori, streptomyces olivochoromogenes, and Bacillus subtilis. Hemicellulases from the first two organisims were more effective than those from the third, Kappa number of unbleached pine and birch kraft pulps were both reduced by 50% from original values by treating the pulps with hemicellulase followed by peroxide treatment.

Table–1

Combined fungal and chemical treatment of Pulp[8].

Initial Brightness=32.7% ISO

Particulars	Control pulps CEDED	C. Versicolor treated pulp (FDED)
Brightness (5 days treatment), % ISO		50.1
Ist Chlorinedioxide stage		
Kappa number	0.9	4.3
Brightness, % ISO	81.7	62.7
2nd Chlorinedioxide stage		
Brightness, % ISO	88.1	82 3
Viscositv,m Pa's	11.2	12.6

Table–2

Bleaching conditionin and optical properties of hardwood and softwood kraft pulp[9].

Particulars	Hardwood KP	Softwood KP
Conventional Bleaching		
Initial kappa number	20.9	40.0
chlorination (c)	5.0	9.0
Alkali extraction (E_1)	3.6	6.4
Chlorinedioxide (D_1)	0 8	1.0
Alkali extraction (E_2)	0.2	0 5
Chlorinedioxide D_2)	0.3	0.5
Total effective chlorine %	7.89	12.95
Brightness %	88.8	84.2
PC Number	0.78	0.38
Biobleaching :		
Bio-treatment	5 days	6 days
Kappa Number after treatment	8.5	14.9
Chlorination (C)	1.4	2.4
Alkali extraction (E)	0.8	1.7
Chlorine dioxide (D)	0.3	0 4
Total effective chlorine %	2.19	3.45
Brightness %	88.1	84.6
PC Number	0.46	0 25

**Chemical dosages was based on % O.D. Pulp.

Table–3

Enzymatically and controlled bleached pulp properties and chemical consumption[14].

Bleaching Sequence	Yield (%)	Viscosity (dm^3/kg)	Brightness (% ISO)	Consumption (kg/t) Act. Cl_2	H_2O_2
Enz. $E_{p1}D_1E_{p2}D_2$ (pH_7)	95.5	1230	83.8	50	5
Enz. $E_{p1}D_1E_{p2}D_2$ (pH_9)	95.4	1230	85 0	50	5
$CE_{p1}D_1E_{p2}D_2$	93.5	1160	88.9	58.75	4.75
$DCE_{p1}D_1E_{p2}D_2$	93.9	1150	88.8	53.2	4.9

There is some potential for bleaching kraft pulp with micro-organisms. For a successful bio-bleaching process, the application of the fungus, which extensively and selectively degrades wood lignin should be considered. Bio-bleaching in combination with conventional bleaching could mean saving in chlorine or even the introduction of chlorine free bleaching. Fungi produce delignification of both hardwood and softwood kraft pulps, but the process is slow at present. Understanding the enzymology of the bleaching effect and application of the required enzymes should result in a faster rate and a more acceptable pulp product.

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