Emerging Applications Of Enzymes For Energy Saving In Pulp & Paper Industry

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ABSTRACT

The pulp and paper industry is an energy-intensive process industry where energy contributes 18-25% of the manufacturing cost. Due to shortages in energy availability and increase in energy cost, energy conservation has become a necessity in the paper industry. Any process that significantly decreases the energy requirement in the pulp and paper process will have a significant beneficial effect on the overall energy input. Recently, there has been increased awareness of biotechnological processes, especially enzymatic processes in the pulp and paper industry to reduce the energy consumption and improve the product quality. The emerging applications of enzymes like pulp bleaching, refining of pulp to reduce the refining energy and improve the papermaking process and product, drainage aid to reduce energy and increase paper production capacity, enzymatic deinking, enzymatic pretreatment of wood chips/ other raw materials for mechanical and chemical pulping to reduce energy/ chemicals and improve pulp yield and quality, enzymatic removal of extractives to reduce pitch problems, enzymes in removing shives and vessels, in stickies control, etc. have great potential in pulp and paper industry.

Introduction

In general, the pulp and paper industry is highly energy intensive. The global paper industry is the fourth largest consumer of primary energy in the industrial sector, with an annual primary energy consumption estimated at 8 EJ, of which 2.3 EJ are from wood waste and black liquor (non-conventional energy) [1]. On the basis of average specific energy consumption (SEC) of papermaking only, excluding pulping is about 3.1 EJ. SEC is affected by the nature of the energy used as well as by paper grade. In the U.S., the pulp and paper industry has reduced energy use about 42% during the period 1975 to 2005 (as per Intermediate Energy Infobook 2007). The SEC in Indian pulp and paper industry is 33.7-47.7 GJ/ton. The average SEC (GJ/T) was 60 in 1987, reduced to 51 in 2002 and to 40 in 2009 whereas it is 23 GJ/T by best available technology (BAT) [2]. In India, the pulp and paper industry has been the sixth largest consumer of energy in the industry sector. The energy cost as a percentage of manufacturing cost has increased from 15% in 1979-80 to about 24.5% in 1992-93 and to more than 25% by 2009. This is mainly due to increase in energy prices. However, the Indian pulp and paper industry has reduced the energy usage by more than 33% during the period 1987 to 2009. At a time when energy costs the world over continue to skyrocket; energy conservation techniques come as a welcome relief.

The average green house gas emission is 2.5 ton CO_2 per ton of paper production, which is quite high as compared to BAT. By reducing the SEC, the consumption of fuel will also reduce, resulting in the reduction of CO_2 emission as well. The options available for reducing the energy consumption are:

1. Starting points for reducing energy consumption and energy costs:
   - Savings due to procurement of energy (fuels, electricity)
   - Savings by optimizing the existing plants (heat and power generation, distribution networks, products plants)
   - Saving by optimizing the papermaking (generating and production plants)

2. Generation and use of heat & power
   - Operation of combined heat and power (CHP) systems to provide steam and electricity
   - Increased cogeneration and additional use of waste out of production and refused derived fuels
   - Heat integration / use of pinch technique

3. Optimization, control and new technologies
   - Better control of various operations and by maximizing the utilization of existing plants/ equipment
   - Change over to energy efficient technologies very often, capital intensive

Recently, awareness of biotechnological processes, especially the enzymatic processes, for energy conservation has increased in the pulp and paper industry. It involves the enzymes to make or modify a product for commercial use.

Enzymatic Processes

Enzymatic processing offers potential opportunities for changing the industry towards more environmental friendly and efficient operations compared to the conventional methods. The main advantages of enzymatic processes are: they are highly specific in action, require milder conditions, conserve energy, generate less pollution than chemical processes, improve product quality, and very often require very low capital investment.

Following are the emerging applications of enzymes that have great potential and are being established: bleaching of pulp, beating & refining of pulp, drainage aid, deinking, mechanical or chemical pulping and others like removal of shives, reduction of vessels in tropical hardwoods,

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removal of extractives from pulp, stickies control, etc.

Bleaching of pulp

Pretreatment of pulp with xylanase enzymes has proved to be cost effective way of bleaching for mills to realize a variety of bleaching benefits including reducing the use of chlorine, decreasing AOX discharges, freeing up chlorine dioxide generating capacity, or increasing the brightness ceiling. Results from mill applications show about 20-30% reduction in active chlorine at the chlorination stage for hardwoods and 10-20% for softwoods whereas savings in total active chlorine were found to be 15-20% for hardwoods and upto 15% for softwoods if the pulps were pretreated with xylanase enzymes [3, 4]. It has been shown to be easily applicable with existing industrial equipment, which is a considerable advantage of the technology. The enzymatic reaction takes place during the storage of brown stock in the high-density storage tower and does not require any additional stage of bleaching. Thus, an appreciable amount of energy used in operating an additional stage of bleaching is saved.

Table 1. Primary energy flows related to use of xylanase enzyme for treating one tonne pulp

Enzyme/ chemical	*Amount (kg)*	*Primary energy*		*Comments*
		Specific (MJ/kg)	*Total (MJ)*	
Xylanase enzyme	0.75	22.5	16.88	Induced
Chlorine dioxide	4.00	117	468.00	Avoided

If we consider the saving in primary energy, it is phenomenal. For example, in one case of ECF bleaching, the chlorine dioxide saving was 20% or 4 kg/ton pulp by using 0.75 kg of xylanase enzyme formulation [5]. The induced primary energy through enzyme is about 17 MJ/T pulp (the production energy for xylanase enzyme formulation was 22.5 MJ/kg) and avoided primary energy was 468 MJ/ton of pulp (the production energy for chlorine dioxide is 117 MJ/kg) (Table 1). The difference between the induced and the avoided primary energy consumption was more than 450 MJ/T of pulp. This also means that when 1 kg of xylanase enzyme is used, around 600 MJ of primary energy is saved.

Pulp bleaching with lignin oxidizing enzymes is also being explored [6]. These enzymes, unlike xylanase, attack lignin directly and hence are more effective and there is no damage or loss of cellulose resulting in better strength and yield of bleached pulp. The most important lignin oxidizing enzymes are lignin peroxidase, manganese peroxidase and laccases. Several reports suggest that the laccases have great potential and could prove useful in bleaching. Treatment with laccase enzyme requires milder conditions and results in more removal of lignin than oxygen delignification, which translates into substantial savings of energy. However, due to requirement of a mediator for laccase enzyme to work, the process has reached to pilot scale only - still not been commercialized.

Potential of lipase enzyme for pulp bleaching has also been explored. In a study, a commercial lipase enzyme has been evaluated for kraft pulp bleaching [7]. It has been reported that lipase promotes better delignification efficiency as compared to xylanase. Lipase shows specificity to remove hexenuronic acid (HexA). However, some accessory enzymes like feruloyl esterase, arabinofuranosidase, glucuronidase and hexenuronidase along with lipase give better results in terms of HexA removal, bleaching and BOD of bleaching effluent.

Refining of pulp

Interest in the use of enzyme as a way of modifying fibre properties to improve the beatability and refinability of pulps has increased mainly due to the availability of mild and non-aggressive enzyme activities (e.g., from *Chrysosorium sp.*) [8] that do not affect the pulp properties and yield, unlike earlier enzymes from *Trichoderma sp.*, which did affect the pulp properties [9].

The use of cellulase and hemicellulase enzymes can also help in saving energy if an enzymatic treatment is carried out before beating and refining [10-13].

Enzyme produces a better fibrillation so those paper properties that depend on fibril content turns to be better. These properties are tensile strength, bursting strength & T.E.A. Enzyme partially eliminates fines, mainly those contained in the white water loop, turning the recycled water to be cleaner and permitting to achieve the right content of fines. This produces additional effects such as an increase in paper machine speed, decrease steam load for paper drying and reduce vacuum. Enzymatic treatment can also help in de-bottlenecking of refiner capacity to increase the production and possibility of utilizing difficult to refine pulp. It could also lead to better biodegradability of machine effluent and ease in operation of ETP: Improvement in BOD/COD ratio in mill wastewater is also expected to increase. Enzymes partially hydrolyse fines and cellulosic debris to low molecular weight saccharides (C2 to C12) that are easily biodegraded in the wastewater treatment system. By saving the refining energy, it reduces the green house gas emissions associated with generation of steam and power.

Case studies on process scales:

The saving in electrical energy of the order of 25 kWh/T of pulp in refining and reduced steam requirement (about 0.6 T/T of paper) in drying of high strength ESKP produced by long fraction of bamboo pulp pretreated with imported enzyme was obtained on the process scale [10]. Most of the strength properties remained almost unchanged. In a similar process scale trial during the production of coated base paper, electrical energy savings were 70 kWh/T of softwood pulp and 30 kWh/T of MTH pulp (Table 2). The reduction in steam requirement for drying of

Table 2. Effect of enzyme treatment* on power and steam consumption during coating base manufacture - Process-scale trial results (*based on ref.10*)

Particulars	*Power consumption (kWh/T pulp)*		*Steam (T/T paper)*
	Softwood	*Hardwood*	
Control (no enzyme)	200	150	2.57
Trial (with enzyme)	130	120	2.07
Savings	70	30	0.50

**Conditions: Temperature, 40-45^{0}C; pH, 6.8-7.0; Enzyme dose 100 g/TP (in both the streets)* paper was 0.5 ton/ton of paper.

In another process scale trial with indigenous enzyme, it was possible to bypass one TDR in the production of high gsm base paper when the pulp was pretreated with enzyme.

The enzymatic treatment of pulp, before refining, is expected to give more benefits to those mills, which are not having captive power generation and/or limited by refining capacity. This is expected to give further benefits by way of savings in the maintenance cost of the refiner or the mill can produce more paper without augmenting the refining capacity.

Drainage aid

Recycled fibres have lower strength and higher drainage resistance than virgin fibres, which limit the paper quality and the speed at which machines can operate. The mechanical properties of fibres as well as their ability to swell are diminished after they are exposed to pulping and drying conditions imposed during the paper making cycle. Freeness reduction during beating is much faster for secondary fibres. The fines created, when secondary fibres are beaten, consist largely of microfribils that were strongly coupled to each other when they were originally dried on the paper machine. When liberated during refining, they increase the specific surface area of suspension more than the swelling potential. They start to behave as fillers, with a small effect on strength but a large effect on the drainage properties. In general, the greater the degree of refining of the virgin fibres, the lower is the recovery potential of sheet properties that are a direct function of fibre bonding such as burst strength and tensile strength. Sheet density decreases each time the fibres are recycled. The strength losses may be the result of loss in binding potential, either in the strength of the inter-fibre bonding or in their number.

The potential of improving the drainage rates of recycled fibres by cellulase mixtures was discovered in the late eighties [14]. Researchers from La Cellulose du Pin were the first to show that a mixture of cellulase and hemicellulase enzymes increases the freeness of pulp. Improved drainage and faster machine speeds resulting from increased freeness, yields significant savings in energy and thus in overall cost. The endoglucanase activity is a prerequisite for drainage improvement of recycled pulps.

Several commercial enzymes are available which improve the drainage of secondary fibers. A commercial cellulase enzyme preparation (Pergalase A-40) based on *Trichoderma* has been used in several mills to improve drainage [15]. These types of enzymes are applied after refining/ beating of the pulp, mainly to improve the dewatering. Recently, a cellulase enzyme with endoglucanase activity (FiberCare® D) developed by Novozymes has been reported to substantially increase the runnability of recycled furnishes (Fig. 1) and reduces the steam consumption in drying of paper on treating the pulp with enzyme after refining [16].

The virgin pulps made from agri-residues have the problem of low drainage. Treating these pulps with the enzymes after refining of the pulp is expected to reduce the drainage resistance to some extent.

Deinking of used paper

Enzyme assisted deinking has been shown to represent a potential environmentally friendly alternative to conventional alkaline deinking processes [17,18]. In most cases cellulases represent the best choice; however, other enzymes such as hemicellulases, amylases and lipases can help in order to optimize the process depending on the type of paper and ink.

Enzymatic approaches of deinking involve attacking either the ink or the fibre surfaces. Lipases and esterases can degrade vegetable oil based inks. Pectinases, hemicellulases, cellulases, and ligninolytic enzymes alter the fiber surface or bonds in the vicinity of the ink particles, thereby freeing ink for removal by washing or floatation [17].

The potential of combining cellulase enzymes with sulfite deinking to achieve a superior natural deinking strategy for deinking of old news print (ONP)/old magazine paper (OMG) was also examined by Zhang *et al.* [19]. They reported substantial improvement in the deinking performance of ONP/OMG in 70:30 ratio as compared to either cellulase enzyme or sulfite deinking.

Deinking with enzymes at acidic to neutral conditions should reduce the overall chemical requirements and minimize yellowing of reclaimed papers normally observed by conventional alkaline deinking. The use of enzymes could lead to a reduction of the pulping time thus saving energy and potentially increasing production. Besides the greater decrease in the ink area, the mild alkaline conditions used with enzymes impact positively on stickies problem at mill scale. Enzyme treated pulps generally have better drainability, resulting in increased speed of paper machine. An additional positive effect can also be expected as a consequence of non-ionic surfactant reduction due to its slow biodegradation in the water treatment plant.

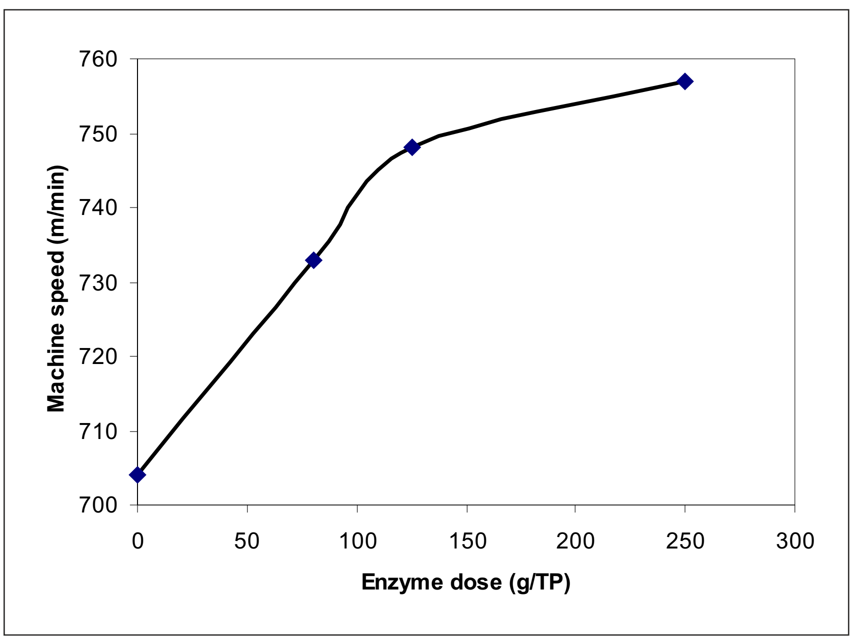

Fig. 1. Effect of enzyme dose on machine speed using OCC and MW pulps to produce 200-gsm liners at a North American mill *(based on ref. 16)*

Case studies:-

The deinked pulp obtained after deinking of sorted office waste with hydrolytic enzymes showed higher brightness (1.0-1.6 points) and whiteness (2.7-3.0 points) and lower residual ink as compared to chemically deinked pulp [18]. It was possible to obtain pulp of <10ppm dirt count with combination of cellulase and alpha-amylase enzymes resulting in reduced chemical consumption. COD and colour loads were lower in case of effluents generated during enzymatic deinking (Table 3).

Table 3. Comparative performance of deinking using conventional and enzymatic processes (*based on ref. 18*)

Sr. no.	*Parameter*	*Deinking with*	
		Chemicals (control)	*Cellulase + alpha-amylase*
A	**Deinked pulp properties**		
1	Brightness (%ISO)	80.1	81.7
2	CIE Whiteness	69.2	71.5
3	Dirt count (ppm)	16	8
4	Yield (%)	71.1	70.9
5	Ash (%)	6.3	6.2
B	**Chemical consumption**		
1	Enzyme (kg/TP)	nil	0.4
2	Sod. hydroxide (kg/TP)	26.0	16.0 (-10)
3	Sod. silicate (kg/TP)	10.0	0.0 (-10)
4	Hydrogen peroxide (kg/TP)	25.0	20.0 (-5)
5	DTPA (kg/TP)	2.0	2.0
6	Surfactant (kg/TP)	2.0	2.0
C	*Pollutants generation*		
1	COD (kg/TP)	40.7	36.8
2	Colour (kg/TP)	10.5	8.5
Initial brightness 61.1 %ISO, Initial whiteness 53.6, Initial ash 14.2%, Initial dirt count 3000 ppm			

Treatment of 100% multiprints furnishes with cellulase and amylase enzymes at pH 7-7.5 improved the pulp brightness by 2 ISO points in the laboratory investigation as a part of EUREKA Enzyrecypaper Project [20]. The ink particles released on treating with amylase enzymes appeared to be more hydrophobic than ink particles released on treating with cellulose. During the mill trial using highly specific amylases, the brightness was significantly improved up to 8 points. The ash content also reduced to a great extent after flotation and washing, resulting in a change of the final pulp characteristics.

Mixed office waste often contains a large variety of dyed papers. The colour must be removed to make the pulp suitable for reuse. For this reason, it is frequently underutilized source of waste papers. Usually, several chemical bleaching agents like ozone, oxygen, hydrogen peroxide or sodium hydrosulfite have been used to bleach secondary fibers. Now, there is an alternative colour stripping process for secondary fibres the laccase-mediator system. In a study by Arjona *et al.* [21], a bleaching sequence included an enzyme stage called laccase-mediator system stage (L), a hydrogen peroxide stage (P) and a sodium hydrosulfite stage (Y) on a mixture of different coloured writing & printing papers. After the application of L-P-Y sequence, a pulp with optical properties near to eucalyptus totally bleached pulp was obtained. The L-P-Y sequence reaches a colour removal of 90% and saves chemicals in the final stages.

Mechanical or chemical pulping

The energy required in mechanical pulping to refine chips into pulp is typically one of the largest costs of production for mills. Treatment of wood chips with fungus has demonstrated the reduction in mechanical refining energy and also requiring milder conditions for kraft pulping. However, fungal treatment has several limitations like regular supply of inoculum, large scale decontamination requirement of material before inoculation, long incubation period, aeration and temperature control, etc. Therefore, it could not be commercialized so far. On the other hand if enzyme treatment becomes effective, the process implementation will have lesser problems.

Refining power reduction after treatment of chips with commercial cellulose enzymes has been reported [22]. It has also been shown that treatment of coarse TMP pulp with cellobiohydrolase enzyme decreased refining energy in the subsequent refining stages without any adverse effect on optical or physical properties of the resulting hand sheets [23]. Eriksson *et al.* [24] investigated the changes in the structure of the wood and the resulting fibre due to the treatment with a commercial cellulase (having CMC, xylanase, filter paper activities) on different southern wood species. The results varied with the wood species. Maple showed the most improvement in fibrillation after enzyme treatment of the three wood species investigated. Pine seemed to require higher enzyme doses to show appreciable change. Poplar did not show much improvement. Enzyme treatment did not reduce defibering energy during primary refining but provided a higher quality or more defibered pulp with energy saving in the secondary refining stage. Specific energy reductions of up to 25% or 500 kWh/TP were observed on pretreating the European poplar chips with xylanase enzyme relative to untreated controls [25]. Enzymatic treatment before mechanical pulping has limitations of enzyme diffusion into the chips. The enzymes are expected to give appreciable saving in secondary refining if the treatment is given after primary refining. In case of bagasse, which has open cell walls due to crushing of cane, enzyme treatment is expected to give much better results even in the primary refining stage.

Chemical pulping of enzyme treated raw materials, especially agri-residues like bagasse, will also require milder conditions (reduced cooking time/ temperature/ chemicals: energy savings and or increased capacity) and expected to give better quality and yield of the pulp. Investigations are being carried out with the wood chips also to improve the chemical pulping process by enzymatic pretreatment of chips.

Other applications

Removal of shives:-

Generally, more bleaching chemicals are used for removing the shives from the pulp. Some enzyme formulations can remove the shives after bleaching if the pulp is treated with the enzyme before bleaching [26]. Enzymatic treatment helps to remove shives from the pulp beyond the associated gain in the brightness. Removal of shives and ease of pulp bleaching by the use of enzymes also helps in reducing the energy requirement, as the bleach chemical dosing is not increased in this case to remove the shives.

Reduction of vessels in tropical hardwoods:-

The vessel elements of tropical hardwoods are large and hard and they do not fibrillate during normal refining. As a result, they stick up out of the surface of the paper. During printing, the vessels are torn out, leaving voids. This characteristic reduces the value of tropical hardwood pulp. Although increased beating can eventually increase vessel fibrillation and flexibility, it can also result in poor drainage in addition to extra energy requirement for beating/refining. Treatment of pulp with cellulase enzyme can enhance the flexibility of hardwood vessels. Vessel picking reduction by 85% along with improved drainability, smoothness and tensile strength have been obtained [27]. This way, enzymes can result in energy savings in beating of vessels.

Debarking of wood employing enzymes [28], *removal of extractives* (pitch) from the pulp using enzymes [29] and *stickies control* in recycled pulp with the help of enzyme [30] are other applications of enzymes in pulp & paper industry. All these enzymatic processes reduce the requirements of energy.

Environmental Aspects

The average green house gas emission is about 2.5 T CO_2/T of paper production, which is quite high. By reducing the specific energy consumption in pulp and paper making, the consumption of fuel will also reduce, resulting in the reduction of CO_2 emission as well.

A study has shown that fossil energy consumption and potential environmental impacts (global warming, acidification, nutrient enrichment, photochemical smog formation) induced by enzyme production are low compared with the impacts that they save when applied in bleach boosting, refining, drainage improvement, deinking, mechanical or chemical pulping and stickies control, etc [31]. The general explanation is that small amounts of enzyme provide the same function as large amounts of chemicals and that enzyme production and enzymatic processes generally require less fossil energy inputs than conventional processes.

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