Use of Carbohydrate Modifying Enzymes in Papermaking

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ABSTRACT

This paper deals with the application of carbohydrate-modifying enzymes in improving the dewatering of pulp and reducing the energy requirement in refining/ beating. Few case studies are also included. Upto 30% improvements in drainage have been observed on treatment of recycled fibre with commercial enzymes having endoglucanase activity. Similarly, 20-30% reductions in energy requirements for refining of pulp are noticed on pretreating the pulp with enzymes having cellobiohydrolase (CBH) activity.

INTRODUCTION

Carbohydrate-modifying enzymes, specifically cellulases and hemicellulases have found useful applications in bleaching, fibre modification and deinking. In these applications, a minor part of the carbohydrate is removed. In fact, enzymes can be used for specific modifications of fibre carbohydrates in order to develop improved processes and products for the pulp and paper industry. Enzymatic methods are usually easy to implement to the industry and represent environmentally benign technologies. Enzymatic methods must, however, be able to compete with existing and developing technologies. Therefore, in comparison with competing technologies, enzymatic methods are most applicable when performing reactions with higher specificity or decreasing environmental impacts and/ or costs.

The major targets of enzymatic modifications of fibre substrates follow the general targets for improving pulping and paper manufacturing processes; i.e. saving of chemicals and energy, improving yields and decreasing environmental loadings. In addition, the product properties can be modified by using enzymes. The most extensively studied and widely used application of carbohydrate modifying enzymes is the bleaching of chemical pulp. These enzymes have also been studied for deinking of recycled fibres (1), improvement of drainage of fibres (2), decreasing energy consumption in refining (3) or modification of fibre properties in specialty paper products (4). The main objectives of using carbohydrate-modifying enzymes in pulp and paper industry are summarized in Table 1.

Improving the drainabilty of fibres and reducing the energy requirements in refining are the two important applications of enzymes in papermaking. This paper deals with the application of carbohydrate-modifying enzymes in improving the dewatering of pulp and reducing the energy requirement in refining/ beating. Few case studies are also included.

USE OF CELLULASE ENZYMES

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, but its organization in the fibre makes it a complex target for chemical or enzymatic modifications. Depending on the type of pulp; i.e. chemical or mechanical, the target site may vary. 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. The molecular size and structure of an enzyme are important factors when considering the limited accessibility of the substrates in fibre matrices. The molecular size of the major cellulase enzyme cellobiohydrolases (CBH I) from Trichoderma reesei, is 65 kDa, and 4.0x5.0x6.0 nm in size. According to this, it is

Table 1 Application of carbohydrate-modifying enzymes in pulp and paper industry

Type of pulp	Target	Enzymatic action on
Mechanical	Energy saving	Cellulose
	Flexibility	Cellulose
Chemical	Beatability	Cellulose
	Sheet properties	Cellulose
	Air resistance	Hemicellulose
	Density	Hemicellulose
	Bleachability	Hemicellulose
Recycled	Deinking	Cellulose + hemicellulose
	Drainage	Cellulose

expected to penetrate most of the pores in chemical pulps. Other factors such as the molecular organization of the fibre components and linkages between lignin and carbohydrate may also have a significant role in the accessibility of fibre bound substrates. As all enzymes first attack the most accessible areas of cellulose fibres, their effects are highly dependent on the type of fibre used and thus the applicability of individual enzymes will depend on their mode of action and the technical aim.

Cellulases have been divided into exo and endo acting enzymes. The widely accepted theory for their synergistic action is the endo-exo model; initially endoglucanases (EG) hydrolyze internal glycosidic bonds randomly in the chains at the surface of the cellulose fibres and thereby produce free chain ends. Cellobiohydrolases split off cellobiose units from the chain ends one by one in an exo like fashion. The positive technical implications derived from the theoretical mode of action of different cellulases are less clear than their negative effects. Due to the importance of cellulose to the fibre strength, the use of cellulases is always a compromise between desired effects and negative side effects.

Table 2 Effect of enzyme treatment on the drainability of low freeness pulp (490 ml CSF)

Enzyme dose, % o.d. pulp	Reaction min	Drainage time for 800 ml, sec	Improvement in drainage, %
0	--	31.5	--
0.1	30	27.8	11.7
0.1	45	26.5	15.9
0.1	60	26.1	17.1
0.1	120	25.1	20.3
0.1	180	23.5	25.4
0.2	30	24.8	21.3
0.2	60	22.8	27.6
0.2	180	21.5	31.7
Conditions: pH 5.0; temperature, 50°C; pulp consistency 5%			

IMPROVEMENT OF DRAINAGE

The use of waste paper (recycled fibre) in paper manufacture has been increasing for last one decade. Its use is expected to grow further due to economic and environmental reasons. 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. For equivalent beating times, a sheet containing recycled fibres is less dense and usually more absorptive than virgin fibre stock. 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. Folding endurance of recycled paper is also considerably lower than for sheets made from virgin stock. 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.

Table 3 Effect of enzyme treatment on the drainability of high freeness pulp (620 ml CSF)

Enzyme dose, % o.d. pulp	Reduction min	Drainage time for 800 ml, sec	Improvement in drainage, %
0	--		--
0.1	45	15.5	Not significant
0.1	120	14.4	7.7
0.1	240	14.1	9.6
0.2	60	13.6	12.8
0.2	120	12.5	19.9
0.2	180	11.8	24.3
0.3	60	11.5	26.3
0.3	180	11.3	27.6
Conditions: pH 5.0; temperature, 50°C; pulp consistency 5%			

The potential of improving the drainage rates of recycled fibres by cellulase mixtures was discovered in the late eighties (5). 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 theoretical endowise action of the endogucanases (EG) of T. reesei enables their use in the fibre structure, such as fines or outer fibrillation fragments. The endoglucanase activity is a prequisite for drainage improvement of recycled pulps whereas CBH has no effect. Several commercial enzymes are available which improve the drainage of secondary

Table 4 Effect of enzyme treatment on beatability and strength properties of unbleached softwood pulp

Enzyme	Reduction in beating time, %	°SR	Tensile index, Nm/g	Braking length m	Tensile energy absorption, J/m	Burst index kN/g
SET - 1						
Control		25	65.68	6699	78.91	5.75
Enzyme 1	22.7	25	66.13	6745	90.41	5.59
Enzyme 2	25.0	25	60.92	6214	68.50	5.20
Enzyme 3	20.8	25	66.55	6788	87.99	5.97
SET - 2						
Control		25	63.79	6507	68.33	5.09
Enzyme 3	19.9	25	63.70	6497	69.77	4.92
Enzyme 4	17.9	25	60.46	6167	60.67	4.84
Enzyme 5	17.9	25	63.91	6519	64.00	5.00

Conditions: temperature, 50°C; pulp consistency, 4%; reaction time, 3 h; enzyme dose, 0.05% on o.d. pulp; pH, optimum for different enzymes - from 4.5 to 7.0

fibres. A commercial cellulase enzyme preparation (Pergalase A-40) based on Trichoderma enzymes is currently used in several mills to improve drainage or to produce release papers or wood containing printing papers (6, 7)). These types of enzymes are applied after refining/ beating of the pulp, mainly to improve the dewatering.

Case study

The effectiveness of several commercial carbohydrate-modifying enzymes was examined for improving the drainage of secondary fibres. Drainage improvement over the control was substantial with Pergalase A-40 (a mixture of cellulase and hemicellulase) when the old corrugated carton (OCC) pulp was treated after refining. The effect of the Pergalase treatment on pulps of different initial freeness showed that the lower the initial freeness, the higher the gain (Tables 2 and 3). The drainage improvement was 11.7% (with 0.1% enzyme) and 21.3% (with 0.2% enzyme) at a reaction time of 30 min for low freeness pulp. An increase of the reaction time to 180 min improved the drainage by 25.4% (with 0.1% enzyme) and 31.7% (with 0.2% enzyme). The pulp retained most of the required strength properties when treated with Pergalase either at 0.1% enzyme addition and a reaction time of 45 min or at 0.2% enzyme addition and a reaction time of 30 min. Increase of reaction time beyond 30 min with 0.2% enzyme resulted in deterioration of strength properties.

When the pulp is treated with enzyme, the freeness increases without any loss of the mechanical properties in the paper, and when mechanical refining precedes the enzymatic treatment, better physical properties are obtained at a freeness similar to the control one. In other words, better physical properties are obtained at an identical drainability. The increase in freeness can enhance the capacity of a secondary fibre preparation plant, increase machine speed or pulp dilution in the head box, and ultimately produce paper of better quality. Conditions must be modified to each particular situation to maximize the freeness increase. In addition to an increase in freeness, regular use of enzymes under optimum conditions may produce beneficial secondary effects such as greater reliability of the paper machine.

Even 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.

IMPROVEMENT IN BEATABILITY

For the development of required pulp properties the pulp is subjected to beating/ refining. The process uses substantial amount of electrical energy to produce paper from wood. In last few years, a lot of interest has been shown in using enzymes for the modification of fibre properties for improving the beatability of pulps. The use of hemicellulose/ cellulose modifying enzymes have been found helpful in saving energy if an enzymatic treatment is given to the pulp before refining/ beating (8).

One of the principal challenges of using enzymes to enhance fibre bonding is to increase fibrillation without reducing pulp viscosity. The pretreatment of pulps with cellulase enzymes having CBH as major activity has been found to result in decreased energy requirements without any appreciable impact on pulp viscosity/ physical strength. This application of enzymes in papermaking is picking up (9).

Table 5 Effect of enzyme treatment on beatability and strength properties of unbleached softwood pulp

Enzyme	Reduction in beating time, %	°SR	Tensile index, Nm/g	Braking length m	Tensile energy absorption, J/m	Burst index kN/g
Control		28	34.05	3473	32.25	2.26
Enzyme 2	15.0	28	34.88	3558	28.90	2.23
Enzyme 3	15.0	28	34.79	3549	27.50	2.21

Conditions: temperature, 50°C; pulp consistency, 4%; reaction time, 3 h; enzyme dose, 0.05% on o.d. pulp; pH, 5.0 with enzyme 2 and 7.0 with enzyme 3

Table 6 Effect of enzyme treatment on beatability and strength properties of unbleached bamboo pulp

Enzyme	Reduction in beating time, %	°SR	Tensile index, Nm/g	Braking length m	Tensile energy absorption, J/m	Burst index kN/g
Control		39	42.05	4289	42.00	2.71
Enzyme 2	19.2	40	43.03	4389	41.33	2.61
Enzyme 3	18.3	40	42.43	4328	39.67	2.55

Conditions: temperature, 50°C; pulp consistency, 4%; reaction time, 3 h; enzyme dose, 0.05% on o.d. pulp; pH, 5.0 with enzyme 2 and 7.0 with enzyme 3

Case study

The effectiveness of several carbohydrate modifying commercial enzymes has been examined in laboratory for energy savings in beating and refining of different pulps. Unbleached kraft pulps of softwood, bamboo and mixed pulp (60% waste corrugated kraft cuttings and 40% unbleached softwood pulp) were treated with enzymes and the results are given in Tables 4 to 6. With softwood pulp, the maximum reduction in beating time was found to be 25% in the case of Enzyme 2, whereas in the case of Enzyme 1, 3, 4 and 5, the reduction in beating time was of the order of 18-23%. The enzyme-treated pulp retained the required strength properties, except in the case of Enzyme 2., where the strength properties of the pulp were slightly affected (Table 4). Treating the mixed pulp with Enzymes 2 and 3 beating time was reduced by 15% in both the cases (Table 5). Treatment of bamboo pulp with Enzyme 2 and Enzyme 3 reduced the beating time by 19 and 18% respectively (Table 6). The strength properties of the pulps were not found to be affected.

One of the paper mills in India, using hardwood as raw material has also taken a small plant trial with indigenous carbohydrate modifying enzyme and observed a direct benefit of reduction in energy requirement by about 100 kWh for refining each ton of pulp. This also resulted in shutting off of one of the refiners. 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. The enzymatic modification 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.

CONCLUSION

Upto 30% improvements in drainage have been observed on treatment of recycled fibre with commercial enzymes having EG activity. A relatively small amount of enzyme is required while the initial effects are largely beneficial; extending the reaction time with a large concentration of enzyme is detrimental. Similarly, 20-30% reductions in energy requirements for refining of pulp are noticed on pretreating the pulp with enzymes having CBH activity. Careful control of reaction conditions is required both with use of cellulase and hemicellulase enzymes. If the reaction with hemicellulase enzymes is not limited and controlled, for instance a large quantity of enzyme is used, loss in hemicellulose content of the pulp takes place. Hemicellulose in pulp plays an important role both in fibre morphology and fibre physics. Retention of hemicellulose increases the pulp yield, improves pulp strength and affects fibre quality. Similarly, with cellulases, if the reaction is not limited and controlled, the fibres will be affected to a much greater extent leading to a reduction of the average fibre length. Thus, a dramatic loss of mechanical properties in the pulp will occur. In extreme conditions, not only do the fines disappear, but the fibres also begin to be destroyed. Obviously, this destruction leads to a dramatic drop in mechanical properties. The key point of this process is, therefore, the control of the progress of enzymatic reaction. New tools for fibre modification are being developed (e.g. see ref. 10) using genetic engineering, which will enable the development of new mono-component enzymes for their applications in pulp and paper industry (e.g. see ref. 11). Then, the present limitations and problems with the enzymes are expected to be overcome to a great extent.

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