Enzymatic Treatment Of Secondary Fibres For Improving Drainage : An Overview

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ABSTRACT

With the depletion of natural fibre resources, mainly forests and ability of fibre to use again, recycling of fibres is widely accepted to produce various grades of paper. It is also found that on recycling, the quality of pulp deteriorates as the recycled fibers have lower strength and higher drainage resistance than virgin fibers due to its exposures to repeated pulping and drying processes. The extent of deterioration depends on the original pulp type and the papermaking process. To solve out the drainage problem, drainage aids mainly chemicals or polymers are used, various studies on enzymatic treatment have also performed which have proved to be a better remedy for treating secondary fibres and thereby improving drainage. This review highlights the progress of application of enzymes in improving the drainage of secondary fibres including various types of enzymes, mechanism of action and their effects.

Most of the nations face the difficult challenge of meeting society's growing demands for paper products while conserving the forests and achieving environmental and economic sustainability. Recycling offers one key to satisfying these demands. Besides being a low cost source of fiber for paper and board manufacture, recycled fibers serve to preserve and economize scarce forest resources, minimize environmental pollution and contribute to water and energy conservation. More than one third of the paper produced worldwide is made from recycled pulp and in the present day context of scarcity of conventional wood based inputs for papermaking with increasing environmental pressures, paper mills are forced into higher levels of system closure and greater utilization of secondary fibers from waste paper. The need for recycling of fiber sources will increase in the future primarily due to ever increasing environmental concerns, a rapid decrease in the number of suitable landfill sites, more stringent EPA guidelines on recycled fiber content, need for sustainable development, market demands and furnish costs.

The incorporation of secondary fiber in paper production affects the final product quality. With each recycle, the quality of the raw materials deteriorates because of the undesirable changes in the properties of the paper produced and the higher drainage resistance of recycled pulps. The first affects inter-fiber bonding and consequently paper strength. The second makes sheet formation more difficult, decreases the papermachine runnability and increases drying energy consumption. Consequently, a process that allows an increase in freeness should be useful in papermachine or mills can gain advantages of increased production and reduced energy consumption by improving dewatering of recycled pulp (1, 2)).

Various attempts have been made to upgrade the papermaking properties of recycled pulps. The presently known methods of improving the drainage or restoring strength of secondary fibers may be grouped as: mechanical treatment, chemical additives, fractionation, blending, chemical treatments, enzymatic treatments and papermachine modifications (1). Nowadays use of enzymes is gaining popularity in pulp and paper industry including drainage improvement of secondary fibres and therefore in providing benefits to mills. Recently, Bajpai P. K. has given a brief review on use of enzymes for recycling (3).

Literature

Secondary Fiber And Drainage Problem

From the technical and mill applications point of view, secondary fiber represents paper or paper board which is being sent to a different paper mill for reuse. Recycled fibers have lower strength and higher drainage resistance than virgin fibers which limit the paper quality and speed at which the papermachine can operate. Higher drainage resistance caused by decreased pulp freeness of secondary fibers is an inherent problem in recycled pulp fibers (4).

Giles A. F. (5) has commented on papermachine drainage. Papermaking involves the removal of water from aqueous slurry (about 0.5% solids) composed of cellulosic fibers, fines and various chemical additives on a wire to form a wet mat that is then pressed and dried to form paper. Drainage is the ease of water removal from pulp i.e. dewatering process. Drainability is the property of pulp by which water drainage occurs at different stages of papermaking process. There is a general consensus that papermachine dewatering occurs in four stages of free drainage under gravity, vacuum assisted water removal, pressing and drying (6).

Reason Of Drainage Problem

Hubbe *et al*., (7) have described about the fibre changes at both physical and chemical level in recycling and papermaking. Due to exposure of pulping and drying conditions imposed during the paper making cycle the mechanical properties of fibers as well as their ability to swell are diminished. This reduces the strength potential of recovered fibers. Contamination and

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age degradation also contribute to the reduced strength of recycled fiber (1). When a fiber is dried, physical continuities in the cell wall are collapsed by high surface tension forces that pull the surface together. These surfaces become hydrogen- bonded, which reduces swelling in the next cycle. In subsequent beating stages, the recycled fiber will not be able to delaminate and swell well as in case of virgin fibers. Freeness reduction during beating occurs much faster for secondary than for virgin fibers because of fines formation which behave like fillers, with a small effect on strength but a large effect on drainage properties (8).

Available Solution To The Problem (drainage aids and their mechanism)

Drainage aids are materials that increase the drainage rate of water from the pulp slurry on the wire. Almost any retention aid is apt to improve the drainage rate, as fines and fillers are removed from the whitewater; which decreases the solids content of the whitewater; consequently, the drainage and retention may be indistinguishable, and the two are usually considered together. The drainage aid also influences the moisture content of the web going to the press section (9).

A number of studies have been performed on different drainage aids chemicals or polymers (1, 6, 10- 14). Some examples of drainage aids are as follows.

1. **p- DADMAC-** Polydiallyldimethyl ammonium chloride
2. **PEI-** Polyethyleneimine
3. **CATPAM -** Cationic polyacrylamide
4. **ANPAM-** Anionic polyacrylamide
5. **Dual polymer system-** It is the combination of poyelectrolytes e.g. PEI + ANPAM and p-DADMAC + ANPAM.
6. **Microparticle system-** These are based on combinations of cationic polymers with anionic microparticles e.g. cationic starch + anionic colloidal silica.

Mechanism of action-

Polymers can act in accordance with two mechanisms (10) as given below, their characteristics are shown in table 1.

Drainage aid	Charge	Mechanism
p- DADMAC	High cationic	Patch flocculation
PEI	High cationic	Patch flocculation
CATPAM	Medium cationic	Bridge flocculation
ANPAM	Medium cationic	Bridge flocculation
Dual polymer system	High cationic	Patch+ bridge complex
	Medium anionic	
Microparticle system	High cationic	Hybrid

TABLE 1: DRAINAGE AIDS AND THEIR CHARACTERISTICS (10).

Patch flocculation-

Interaction between oppositely charged regions on the particles. It is based upon the formation of cationic sites with a high charge density on the fiber surfaces by cationic polyelectrolytes. If there is strong interaction between the particles and polymer, the polymer can be adsorbed in cationic patches on the negatively charged particle surface so that partial charge neutralization takes place.

Bridge flocculation-

Formation of polymer bridges between particles. In this type of mechanism one part of the polymer becomes attached to one or more absorption sites, while its other part extends into the bulk solution. These extended loops and tails can be absorbed onto other particles thus forming polymer bridges.

Many researchers have explored the use of enzymatic treatments for drainage improvement of pulps like cellulases, hemicellulases and also their combination with polymers; studies performed by Bhardwaj *et al.* (1) are shown in table 2 taking drainage additives and one enzyme Pergalase.

Enzymes are complex protein molecules that act as catalysts speeding up the chemical reactions under a narrow range of conditions. The activity of enzyme depends on the chemical and physical environment (i.e. temperature, pH etc.), enzyme dose and reaction time, the type and concentration of the substrate. An enzyme (E) molecule has a highly specific binding site or active site to which its substrate (S) binds to produce enzyme-substrate complex (ES). The reaction proceeds at the binding site to produce the products (P), which remains associated with the enzyme-product complex (EP). The product is then liberated, and the enzyme molecules are freed in an active state to initiate another round of catalysis.

Enzymes Used For Improving Drainage

The reduced dewatering property of the recovered paper is a major problem during paper manufacture as discussed previously. It has been suggested that these problems can be overcome by treating the pulp slurry with enzymes (15- 16).

Researchers from La cellulose du Pin were the first to show that cellulase and hemicellulase enzymes are powerful to cause an increase in freeness of pulp (1). They used a culture filtrate of the fungus *Trichoderma ressei*, which contained a mixture of cellulose and hemicellulose degrading enzymes. Fuentes *et al*., (17) patented a process for improving the drainage capacity of pulp using an enzyme obtained from the fungus. The most commonly used enzymes are cellulase, hemicellulase and their mixture.

Cellulases

Cellulases hydrolyze **β** 1, 4-glycosidic linkage in cellulose chain. Two major types of cellulases are exocellulases and endocellulases. Exocellulase acts on the end of cellulose chains, cutting bonds on the end of fibre by splitting off cellobiose or glucose causing disruption in cellulose hydrogen bonding. Endocellulases act in the middle of cellulase chain causing

Additive	Dose (% OD pulp)	Drainage time for 800 mL, sec	Improvement in drainage, %
Control	-	45.7	-
Percol 47	0.01	31.8	30
	0.03	22.5	51
	0.05	22.0	52
Percol 63	0.01	31.8	30
	0.03	26.9	41
	0.05	23.3	49
Percol 292	0.01	34.6	24
DK SET DHA 1110	0.04	22.0	52
DK SET TP403 (PO506)	0.04	20.5	55
DK SET TP403 (PO710)	0.04	20.3	56
Trueflocks N 10	0.03	34.7	24
Eureka Flock	0.40	38.4	16
Excell Ex. No. 3	1.25	30.8	33
Amphoteric starch (HLL)	1.25	30.9	32
Amphoteric starch (BSIL)	1.25	31.1	32
Pergalase	0.20	27.6	40

TABLE 2: EFFECT OF VARIOUS ADDITIVES AND ENZYME TREATMENT ON DRAINABILITY OF SECONDARY FIBERS (1)

hydrolysis of the accessible cellulose, in a synergistic sequence of events. Microorganisms have grown as powerful source of enzymes and proved to have effective applications in paper industry. The main cellulase producers used are white rot fungus, *Phanaerochaete chrysosporium*, *Aspergillus niger*, *Trichoderma ressei*, *Penicillium funiculosum*, *Chrysosporium lucknowens* and species of *Acremonium, Talaromyces.*

Hemicellulases

Xylanases and mannanases are hemicellulases with different actions. Xylanases (endoxylanases) hydrolyze the 1, 4 **β**-d-xylopyranosyl linkage of xylans. Mannanases (1, 4 **β**-d-mannanase) hydrolyze the 1, 4 **β**-d-mannopyranosyl linkage of D-mannans and D-galacto-D-mannans. Some examples of hemicellulase producing microbes are *Coriolus versicolor, Glionatix trabeum, Trichocladium candense, Trichoderma ressei, Sporotrichum pulverulentum*, *S. Diorphosporum* and species of *Bacillus* and *Aspergillus*.

Amylases

Amylases play a very significant role in the starch processing industries as they hydrolyze starch. Starch is composed of 10- 25% amylase and 60- 85% amylopectin in ratios that depend on the plant source. Both are polymer of glucose but amylopectin is more branched. They are found to be useful in improving drainage.

They are of three types.

- **α- amylase**- hydrolyzes 1, 4 α- glucanohydrolase linkage.
- **β amylase**- hydrolyzes 1,4 **α**-maltohydrolase linkage.
- **Glucoamylase**- hydrolyzes glucohydrolase linkage.

Among these **α**- amylases deserve greater attention due to their thermal tolerance and optimum pH range near neutral, making them ideally suited to the recycled pulp environment.

MECHANISM OF IMPROVEMENT OF DRAINAGE USING ENZYMES

Targeting colloids

Since the presence of fines and highly fibrillated fibers are associated with low freeness, several theories has been proposed to explain the increase in freeness occurring after enzymatic treatment. Pommier *et al*., (2) reported that cellulase likely attacks colloids in the pulp slurry, and as these colloids decrease, the water drains more easily.

Peeling effect on fibers

Lee and Kim, (18) reported that the enzymes act on the surface of fibers, producing a peeling effect. The chemistry depends on the enzymatic effect on fibre in the form of peeling. A limited or controlled peeling effect will remove the small components having great affinity for water and have role in hydrogen bonding potential of the fibres. As a result there will be reduction of the pulp- water interaction and this will allow better drainage of the pulp without affecting the final mechanical properties of the paper. When the enzymatic reaction starts, the peeling effect occurs and results in an increase in the pulp's drainage. This effect is directly related to the fibrillation of the fibers and thus to the specific surface area available for this enzymes to act. On the other hand, as the reaction proceeds the peeling effect becomes too pronounced and does not lead to a improved drainability, indicating that an optimum contact time must be reached to take full advantage of the action of enzymes. If the enzymatic reaction is not limited and controlled, the fibers will be affected to a much greater extent, leading to reduction of the average fiber length as demonstrated by Oltus *et al*. (19).

Action on fines content

If the progress of enzymatic reaction is uncontrolled than in these extreme conditions, not only do the fines disappear, but the fibers also begin to be destroyed, leading to a dramatic drop in the mechanical properties. Bhat *et al*., (8) have verified the finding of Lee and Kim, (18) using dried bleached and unbleached softwood Kraft fiber. Some basic enzymatic treatment has been worked out by Jackson *et al*., (20). These authors used softwood Kraft pulp as substrate and tested a xylanase preparation and two different mixtures of cellulases and xylanases. CSF was increased by cellulase treatment but not by the xylanase preparation, which showed little capacity for releasing carbohydrates from the pulp. Low enzyme dosage results in reduction of fines content, which was related to a flocculation of enzyme proteins similar

Year	Researchers	Enzyme used	Recycled Material used	Major effects on pulp
1988	Fuents and Robert	Cellulases and xylanases	Recycled fibres	An increase in drainage reported by 18 to 20%
1989	Pommier *et al.*	Cellulases + hemicellulases	Old corrugated container and mixed wastepaper (75:25)	Increase in freeness reported from 290 mL to 415 mL
1990	Karasila *et al.*	Hemicellulase	Unacidified deinked pulp	Freeness increased 160 to 182 mL
1992	Fuentes *et al.*	Cellulases or hemicellulase	Recycled cardboard boxes	°SR decreased from 4-10%.
1995	Bhardwaj *et al.*	Cellulases and hemicellulase	Corrugated kraft cuttings and boxes	Increase in drainage was reported by 11- 25%
1995	Stork *et al.*	Cellulases and hemicellulases	Mixed waste paper	°SR decreased from 73 to 63.5.
1995	Sarkar *et al.*	Cellulase and polymers	Shredded miracle boxes, old newsprint (lab furnish)	Increase in freeness was reported from 242 to 572mL.
			old corrugated containers (mill furnish)	Increase in freeness was reported from 230 mL to 578 mL.
1997	Lascaris *et al.*	α-amylase	Fines from backwater of recycling plant	Upto 5% increase in drainage was found.
1997	Bhardwaj *et al.*	Cellulases + hemicellulase	Corrugated kraft cuttings and boxes	Increase in drainage was reported by 40%
1997	Sarkar	Cellulase and polymers	Corrugating medium or linerboard grades	Increase in freeness was reported by 305- 425 CSF
2000	Oksanen *et al.*	Cellulases, Hemicellulase	Lab recycled ECF-bleached softwood kraft pulp	°SR decreased from 39 to 29.
2002	Pala *et al.*	Cellulase	Old paperboard containers (60% kraft paper, 20% fluting, 20% test liner)	53 °SR decreased by 38%.
2004	Dienes *et al.*	cellulases	Lab recycled Dunakraft 90R sack paper	Increase in drainage was reported by 16%.
2009	Shaikh and Luo	Cellulase	old newsprint, Old ccorrugated containers and mixed waste	Increase in freeness was reported by 13-40%.

TABLE 3: MAJOR STUDIES ON ENZYME AND DRAINAGE IMPROVEMENT.

to polymer drainage aids. Higher enzyme dosages led to an increase in the fines content. This increase in drainage may also attribute to the cleaving of amorphous cellulose on the surface of fines. The major studies on enzyme and drainage are summarized in table 3.

Advantages

When using enzymes for drainage improvement it can be stated that the main advantage is better drainage or dewatering on the papermachine. We may take objective either a better drainage or better dewatering, though it is possible to achieve both.

Increased production rate

An improved drainability results in easy removal of water and better papermachine runnability, therefore an increased production rate.

Reduced drying energy consumption

For a pulp having less drainability there will be more water holding capacity of fibres and thus requires more energy for drying operation. Using enzymes better dewatering results in lesser energy for drying operation. Further additional benefits may be possible that are specific to a particular machine or furnish and may include better runnability (wet- web strength), increased refining without production loss, reduced press loading to improve bulk, use of slower draining fiber furnish components.

Contrary to conventional drainage agents that tend to flocculate fibers, fines and fillers, the enzymes act directly on the surface of the fibers and fines to decrease their water- binding ability. In some cases enzymes can be also used in conjunction with the normal drainage agents to significantly increase the pulp freeness. It is also found to be helpful in a better sheet formation and improving the properties of paper.

Challenges

The action of enzymes on the fiber components can result in improved inter- fiber bonding and decreased fiber-water interactions. Although the mechanism is not completely understood. An enzymatic treatment for a particular pulp is still very difficult to develop, because for each pulp, enzyme selection, concentration etc. have to be optimized. If the enzymatic reactions is not limited and controlled, the fibers will be affected to a much greater extent, leading to a reduction of the average fiber length i.e. detrimental to paper properties.

Conclusion

Under appropriately controlled conditions, it is possible to improve the drainability of pulp substantially without loss of mechanical properties by using enzyme in crude or mixture form. Previous studies have shown that residence time of 30 minutes, pH 5± 0.2, temperature 40- 50 °C, pulp concentration 4- 5 % and optimum enzyme addition on pulp, are suitable for enzymatic treatment. The drainage improvement could be used to increase the speed of the machine or to further dilute the pulp at the headbox. Higher pulp dilution, in turn should produce better sheet formation and improve the mechanical properties of paper.

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