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Think Like an Enzyme

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Enzymes can't, in fact, think. They are not even alive. But some of their effects are so selective and potentially useful that the word "smart" often seems to apply to them.

Whereas the chemical/mechanistic roles of different enzymes tend to be highly specific, the practical applications of enzymes, in general, have been highly diverse. The table lists a variety of such applications in papermaking, together with the presumed role of the additive in each case.

Enzymes owe both their effectiveness and their specificity to the detailed structural arrangements of multiply-folded polymer chains (quaternary structure), as well as the specific order of the peptide groups in the proteins. Specific clefts along the periphery of each enzyme seem designed to fit into the vital sections of the target molecules. The energy barriers of various reactions are reduced due to the subtle molecular attractions, often related to acidic or basic sites within a cleft. In addition, flexing of the protein structure can help cleave molecules that fit into certain folds of the enzyme. Important reactions of this type include cleavage of cellulosic glycoside bonds, triglyceride ester bonds, and a variety of others.

Practical Function	Likely Role of the Enzyme
Easier bleaching	Modify chromophores or make them more accessible.
Reduced refining energy	Weaken attachments between cellulose fibrils in the fiber.
Softness improvement	Locally weaken the fiber cell walls.
Other paper properties	Polish fiber surfaces.
Enhanced drainage	Break down cellulosic fibrillar fines.
Reduced cationic demand	Shorten oxidized polysaccharide chains.
Control of wood pitch	Hydrolyze fatty acid ester bonds.
Slime control	Hydrolyze polysaccharide layers protecting slime bacteria.
Deposit removal	Break down the starch or protein acting as binder in deposit.
Enhanced sustainability	Replace oil-based chemicals serving same functions.

Please see **Think**, *page 2*

Enzymatic Strength Development in OCC

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Introduction

Over the last 25 years, the use of recovered fiber to boost mill capacity has increased sharply. U.S. paper recovery grew from 36.8 million short tons/year in 1995 to about 68 million short tons/year currently (nearly 50% recovery) fueled largely by the rising worldwide demand for fiber. This demand is forcing papermakers to develop grades from lower quality mixed paper streams.

To sustain and improve our industry's position, we must improve profitability through dramatic innovations that reduce manufacturing costs and improve the quality of fiber delivered to the paper machine. Beating and refining are mechanical processes that can enhance fibrillation and internal fiber bonding, but there is a limit to their effectiveness. On the other hand, properly applied enzymes can improve the refining process, increase fiber strength, reduce refining time, and increase inter-fiber bonding through more effective fibrillation.

Please see **Development**, *page 2*

Continued from page 1

Think

In order to get enzymes to act in a "smart" manner, papermaking technologists need to do some careful work ahead of time. The type of enzyme needs to be well matched to the kind of chemical reaction that is likely to have the desired effect. The enzyme also needs to be well chosen with respect to the temperature, pH, and other attributes of the system in which it will be applied. Reaction conditions, especially exposure time and dosage, need to be chosen with care. For instance, batch treatment volumes (in the case of discontinuous treatment schemes) need to be calculated based on flow rates and the expected rates of reaction. Likewise, any treatments involving cellulase need to be kept below the levels that would cause excessive harm to strengths of individual fibers.

Creative thinking is also needed as technologists attempt to improve the effectiveness of various enzymatic treatments. There may be potential to save costs or increase throughput by increasing the catalytic activity of a given enzyme. Recent progress is being achieved, in this regard, on several fronts. Some enzymatic systems become more effective in the presence of certain surface-active agents. In other words, the surfactants are acting as accelerators. Another way to enhance enzyme effectiveness is to recover them, after the exposure period, and return them to an earlier point in the process. Through genetic engineering it is often possible to modify the electron densities at critical points within the clefts of enzymes. The folded structure of the enzymes can be fine-tuned by judicious substitutions of amino acid groups. Recent progress in biotechnology has speeded up the process of screening enzyme candidates in an attempt to find promising variants. Enzyme scientists also construct hypothetical 3-D structures of enzymatic ultrastructures, helping them to select promising approaches.

It has been said that only the paper wasp can make paper in the absence of technology. But nobody claims that they do it without enzymes.

Continued from page 1

Development

Refining is a mechanical process that involves the crushing of the wood fibers between rotating surfaces. This causes the hollow fibers to collapse and flatten. Refining also produces many smaller fibers to extend from the surface of the wood fiber. Since sheet strength is derived from hydrogen bonding at the fiber surface, this flattening of the fiber and fibrillation of its surface give an exponential increase in the amount of surface area where bonding can occur, and are essential in forming the sheet of paper.

Refining requires significant energy input, as well as capital investment. Reducing the need for mechanical refining could provide numerous benefits. *(See table below.)*

Effects from Enzyme	Resulting Benefits
Increases strength of paper sheet by improving inter-fiber bonding	Improved quality
	Increased use of recycled fiber
	Elimination of chemicals used for sheet strength
	Improved softness in tissue
	Allows production of paper requiring very intense refining
Increases strength, allowing reduction in sheet weight	Reduced use of wood pulp
	Reduced pressure on natural wood resources
Can reduce sheet porosity	Reduced use of coating chemicals
Reduces energy required for refining fiber	Reduced need for energy production
	Economic benefit to mill
	May eliminate need for investment in new refiners
Improves other paper qualities	Improved printability, porosity, formation, etc.

Enzymes in the Paper Industry

Since environmentally friendly processes are becoming more popular in the pulp and paper industry, biotechnology is coming to the forefront of research. Biotechnology is defined as the use of biological organisms/systems and processes for practical or commercial purposes, and encompasses a diverse array of activities including fermentation, immobilized cell, and enzyme technology.

The attractiveness of biotechnology lies in its potential to increase specificity in reactions, to provide more environmentally friendly processes, and to save energy and thereby decrease cost. The possibilities for employing biotech in forest-based industries are numerous since one of nature's most important biological processes is the degradation of lignocellulose materials found in wood and its components.

Enzymes are biological catalysts that facilitate a variety of reactions. Advantages of enzymes include their high selectivity, reaction speed, and efficiency. The number of enzyme applications in pulp and paper manufacture has grown steadily. Several enzymes are commercially available for various uses such as xylanases for bleach reduction and brightness increase, lipases for pitch control, esterases for stickies control, amylases for starch modification, proteases for microbial and biofilm control, and more recently cellulases and hemicellulases for fiber modification.

Enzymatic Fiber Modification

Wood fibers are composed mainly of cellulose and hemicellulose microfibrils encrusted in lignin-carbohydrate matrices. They are multi-layered structures that can have internal delamination and external fibrillation after chemical and/or mechanical processing.

Wood pulp can be treated with enzymes, and some of the cellulose in the fiber is hydrolyzed. This biochemical treatment reduces the amount of mechanical treatment needed to reach the desired fiber properties. Less mechanical action and less energy are required. Since refining requires significant energy input as well as capital investment for equipment, helping the refining process could provide numerous benefits, including stronger paper, more use of recycled paper, elimination of other chemical additives, reduced energy usage, and improvement in various tissue properties.

Mill applications prove the benefit of enzyme technology. Some of the advantages are increased paper sheet strength, manufacture of paper with less fiber, and savings in raw materials and natural resources. Also, with this increased strength more recycled fiber can be used. Additionally, less petroleum-based chemicals are required to give strength to the sheet. In some cases, enzymes can be used in place of purchasing additional equipment for refining. In some situations the product directly contacts food, and its use is preferred because of the enzyme's nontoxic nature. Enzymes are a very attractive green chemistry produced from renewable resources and completely recyclable.

Laboratory Studies

Each enzyme in nature is very specific as to what substrate it will act upon. Even within the cellulase family of enzymes, different enzymes react differently with different types of fiber. Cellulases can be categorized into two broad classes—exocellulases and endocellulases. Exocellulases cleave cellulose polymers from the terminal points, while endocellulases randomly cleave bonds along the cellulose chain. Depending upon many factors, including wood species, pulping processes and others, various enzymes will have varying degrees of activity on fibers. So, due to the differences in enzymes and fiber types, enzyme selection must be carried out carefully.

In order to select the appropriate enzyme for a particular application or fiber type, several enzymes are chosen for each test. The pulp suspensions are treated with these enzymes and allowed to react under appropriate temperature conditions for one hour. At that time, the enzyme reaction is stopped with bleach.

At this stage, fiber is refined in a PFI mill laboratory scale refiner. Normally, several levels of refining are chosen so that a refiner curve can eventually be developed. Freeness levels are measured and recorded, and handsheets are made with the remaining fiber. Based upon the typical dry end test parameters of the subject paper mill, dry end testing is then performed. Tensile (including standard and short-span) as well as tear, burst, compression, and other tests can be performed in order to determine the enzyme's effect on the fiber.

An example of the specificity of the enzymes can be seen below. In Figures 1–3, OCC furnish was treated with four different enzyme solutions.

Results of the CSF testing are given in Figure 1. CSF for the samples treated with enzymes A, B, and C were close to the control sample; however, the enzyme D treated sample had a 14% reduction in CSF. This indicates that the action of the enzyme on the fiber has reduced the refining energy requirement. The tear strength comparison (Figure 2) indicated no difference with enzymes A–C. Treatment with enzyme D resulted in a 12% tear decrease. This is in agreement with the reduction in CSF associated with this enzyme. There was an 11% increase in ring crush associated with enzyme D treatment (Figure 3, *page 4*).

Figure 1.

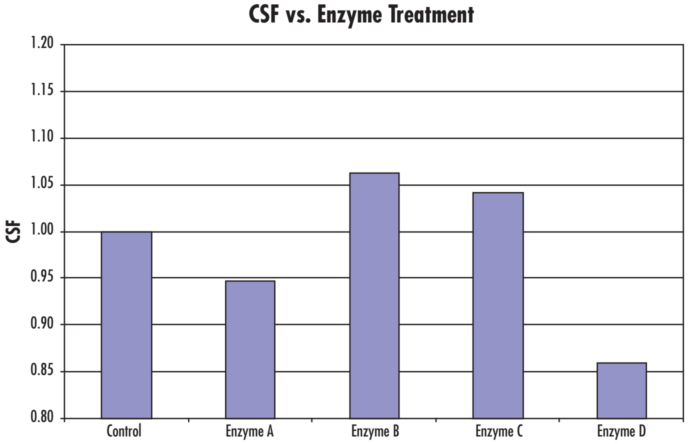


Figure 2.

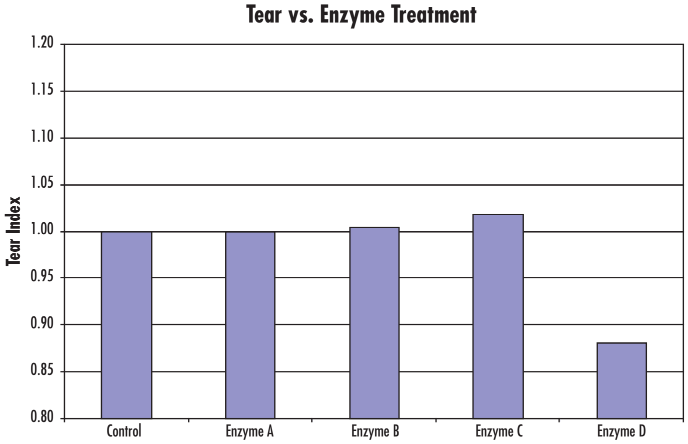
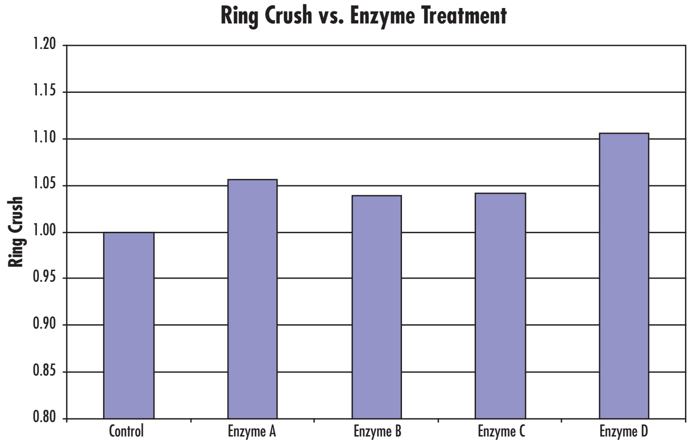


Figure 3.



Mill Application

While the laboratory testing above is exciting, actual application in a paper mill is the only way to determine the validity of the theory and laboratory tests. We have now an ongoing application in OCC, and several other evaluations are underway.

A North American mill producing kraft paper currently uses virgin fiber to meet specs. The Fourdrinier machine runs at 1200 fpm producing 100–140 tpd of 40–100 pound grades. The mill uses 100% OCC but has been struggling to meet specs due to the poor quality of the recycle they are getting, and are employing virgin and/or dry strength additives to meet quality.

BLX 13090 was the product selected in the lab. During the initial evaluation on a 40# kraft, we achieved a significant increase in mullen (32%), and tear was decreased by around 1.8% in both MD and CD directions. To compensate for decreasing tear, the refiner was turned down by 20% and tear came back into specification. Drainage was increased and the machine was able to speed up by 50 fpm.

A second evaluation was run on 84# grade and again we saw similar results. In addition, the mill got very positive feedback from the converter regarding the first evaluation production.

The mill is running the enzyme full time without having to use any virgin fiber and achieving better quality than before.

Concluding Remarks

There are a number of steps involved in running an effective enzymatic fiber modification program. First, determination of the desired outcome is critical. By choosing the end result first, the second step, laboratory work, can be applied more effectively. Do you want higher tensile strength, reduced energy consumption, a higher degree of softness in tissue? Which aspect of fiber modification will best fit your marketing plan?

The second step in determining the appropriate lab work is in understanding the papermaking process. Are the fiber streams refined separately, together, or not at all? What temperature or pH limitations are there that might affect enzyme performance? All of these will determine how the lab testing is performed.

After product determination, the next step is trial planning. Keeping the end result in mind, the trial plan should include the variables that will be used to take advantage of the fiber modification. These variables can include anything that a mill would typically change in order to take advantage of this easier to refine fiber source.

While there will be some time in development of all of this information and learning how to run these programs, the end result for the papermaker is going to be substantial. Since energy costs are escalating, small changes in paper quality can affect the ability to participate in a particular market. Depending upon current fiber pricing, having the flexibility to rationalize fiber sources will have significant financial impact on the papermill's bottom line.

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