ISSN: 0379-5462
IPPTA: Quarterly Journal of Indian Pulp and Paper Technical Association
Vol. 30, E1, 2018, pp.24-26

Bleaching Enzymes – Back from the Drawing Board

Thomas Holm

Buckman Asia Pacific

Man has used enzymes since the first batches of beer, wine and cheese were made thousands of years ago. Our bodies use enzymes for the digestion of food amongst a myriad of other things to survive and to grow. In 1833 Anselme Payen was the first to discover an enzyme. Eduard Buchner received a Nobel prize in 1907 for his discovery of "cell free fermentation," which was in fact, the use of an enzyme. The first commercial enzymes were produced by Röhm in 1914 for the detergent industry. This trypsin enzyme, isolated from animals, degraded proteins and was used as a detergent. It proved to be so powerful compared with traditional washing-powders that German housewives' suspicions were aroused by the small size of the original package, so the product had to be reformulated and sold in larger packages [1]. It has only been in the last 30 years that the paper industry has stepped into the arena. This paper deals with the use of enzymes in the bleaching of wood fiber, its past, its present and its future.

Enzymes are proteins which act as catalysts in either accelerating or inhibiting specific chemical reactions. They are derived from living organisms, yet they themselves are not living. They do not reproduce, nor are they capable of mutation. They can be deactivated under certain conditions and can be destroyed under other conditions. Typically, most enzymes are destroyed at temperatures around 115ºC (220ºF).

The concept of using enzymes in Pulp and Paper first appeared on the scene in the late 1980's. The idea remained in the purvey of research facilities and academia until the late 1990's. It was at this time, the Pulp and Paper Industry was confronted with the issue of dioxin formation in the effluents of some bleach plants. Dioxin formation in the bleaching of wood pulp via the use of chlorine was documented, and the push was on for TCF and ECF bleaching. The industry quickly adapted and began to use chlorine dioxide, which was found to be much less of an issue in the formation of dioxin and readily available. The issue with chlorine dioxide was its cost. In response to this economic disadvantage, the industry quickly adopted the use of oxygen delignification to reduce chlorine dioxide usage. In an effort to reduce chlorine dioxide usage even further, investigation began into the commercial viability of the concept of using enzymes in the bleaching of pulp.

During the early 2000's, mill trials began using a blend of xylanase and cellulase enzymes in an effort to reduce the amount of expensive chlorine dioxide. The industry encountered issues in that, in order for the enzymes to work, a very narrow operational band of pH and temperature had to be maintained over a period of 1-3 hours in order for the enzymes to be effective. Unfortunately, the required conditions were not native to the typical pulp mill, so extensive pH and temperature control strategies had to be employed. It was in the pH control that the bulk of the difficulties were encountered as the typical pH at the end of the brown stock washing system was somewhere between 9.0-11.5. This required extensive acidification at the end of the brown stock washers to achieve the required 6.5-7.5 pH range. The acidification of this pulp proved to be problematic as residual lignin, not washed out in the system, would reprecipitate causing more issues than could be overcome with the enzymes. There were also significant safety issues as hydrogen sulfide gas would be released. Some mills had limited success, but for the most part, the concept of bleaching enzymes was abandoned. For the mills that could implement the process, there were issues with substantial yield loss through the bleach plant. The issue was with the quality of the enzymes as many contained a significant amount of cellulases which caused breakdown of the cellulose along with the hemicelluloses.

In the past few years, the technology of enzyme isolation and production has changed to the point where the new generation of materials warrants a closer look. Through careful manipulation of the biology producing the enzymes, not only have we been able to produce enzymes that perform in a higher pH regime, but we also have been able to purify these materials and remove the unwanted side effects caused by the cellulases. As shown in Figure 1, these new enzymes can operate at pH up to 10.0 and at much higher temperatures and much shorter retention times than their parents and grandparents. This is opening up a new opportunity to not only reduce bleaching costs through the reduction of expensive chlorine dioxide, but also to produce a less toxic effluent through the reduction of chloro-organic compounds, some of which are measured as AOX.

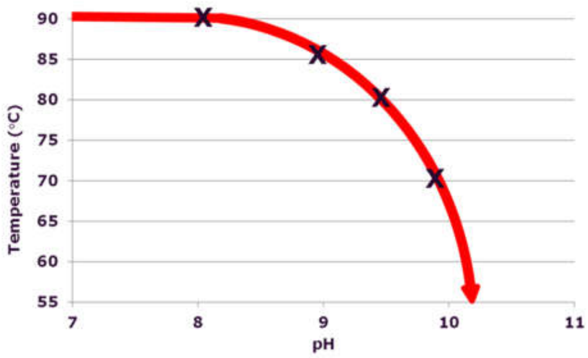

Figure 1: *Effectiveness rage of modern bleaching enzymes*

This new generation of enzymes is now being applied in the pulp bleaching industry with excellent results. Several mills have commercially adopted the technology, and it is used on a continuous basis. The dissolution of xylans before bleaching allows a mill to remove additional lignin compounds attached by a hemicellulose matrix and wash them out of the system before the introduction of expensive chlorine dioxide. In many cases, mills are experiencing a 10-15% reduction in total chlorine dioxide usage, and in some cases, as high as 20%. In addition, the removal of lignin and ferulic acid associated with xylans is assisting in the reduction of the "b" value (or yellowness) of the final pulp [2]. The bluer sheet results in the reduced usage of optical brighteners in the final paper product. The dissolution of xylans has also been shown to reduce overall brightness reversion; therefore, less bleaching chemical is needed to maintain brightness targets.

With all new technologies, there comes a concern for detrimental unintended consequences. If we are removing hemicellulose, we must surely be causing a reduction in bleached pulp yield. While removal of xylan on the fiber surface is the mechanism by which enzymes work, we are only impacting surface xylan and not the cellulose fiber itself. These proteins are large molecules, and stearic interference prevents them from penetrating the fiber wall. One must look at the selectivity of enzymes versus the selectivity of chlorine dioxide in total. If we are to bleach with a very selective chemical such as chlorine dioxide to achieve a high brightness, we will still have to sacrifice some cellulose along with the removal of the hemicellulose to reach our goal. If we introduce an enzyme which can only impact hemicellulose and has no impact upon the base cellulose, we should achieve, at worst, a similar bleaching yield with a pulp that has a much higher brightness and lower reversion characteristics. In real-world applications we have seen no measurable effect on pulp yield.

There is also concern about the impact of the removal of xylans with regards to final paper properties. There are many theories and hypotheses as to what the true impact is by removing xylan, some of which are contradictory. This is outside the scope of this paper; however, multiple mill trials have shown that xylan removal by enzymes has no significant impact on paper properties. A sample of beater curves, with and without enzymes are attached for the reader's review in Figure 2. Time and time again, the results are essentially the same. The removal of surface xylans has had no significant impact upon paper properties. End user characteristics in graphics papers have also been studied, and no ill effects have been found from paper produced from enzymatically treated pulp.

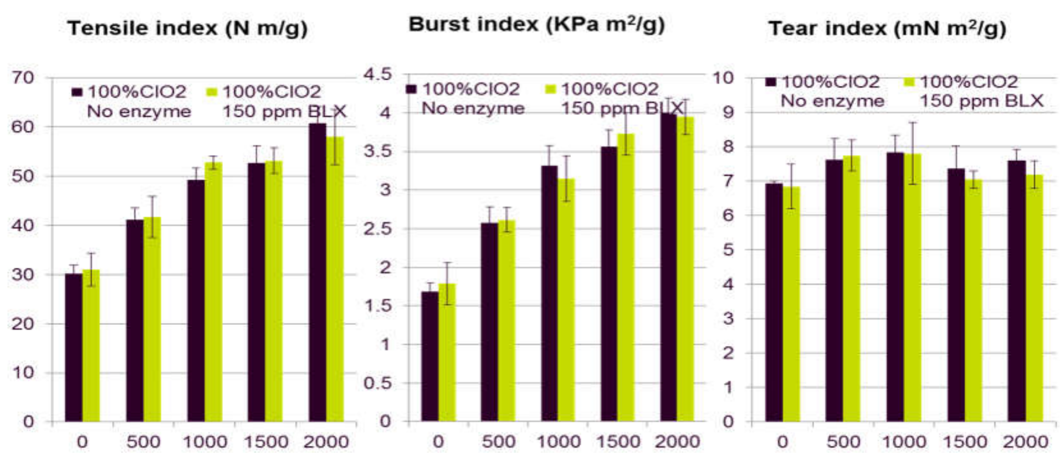

Figure 2: *Impact of enzymes upon standard beater curves (PFI revolutions)*

Another concern with the use of enzymes is the release of additional BOD/COD to the wastewater treatment plant. Enzymes do increase the release of organic material, and in a modern mill where there is a prebleached washing stage, this organic loading is sent back to the recovery system and increases energy content of the black liquor. The net impact in these systems is a reduction in BOD/COD from the bleach plant to the wastewater treatment system. One mill has seen a 14% reduction in effluent BOD where another mill has reduced COD loading to the wastewater treatment plant by about 10%. In cases where there is no prebleached washing, enzyme activity will cause an increase in BOD/COD loading; however, it should be pointed out that the increase is in the form of simple sugars and related organic acids. These materials are much easier to digest than chlorinated phenolic compounds created in conventional bleaching. In fact, at least one mill has taken advantage of this mechanism to reduce the loading of their recovery boilers in order to increase production while having a neutral impact upon the effluent discharge quality. Since we typically see a 15-20% reduction in ClO_2 usage, the effluent from the bleach plant has a lower toxicity. The net result in the effluent quality from the wastewater treatment plant to the receiving body is typically not adversely impacted; however, this must be closely monitored during mill trials. There have been cases, especially when a mill has no prebleached washing and an overloaded activated sludge treatment system operating close to their permit discharge limits, that the additional COD load could not be tolerated. One should also remember that by removing oxidant (i.e. ClO_2), by definition, we will naturally have a higher COD/BOD content in the effluent.

References:

1. Industrial Use of Enzymes -Matti Leisola, Jouni Jokela, Ossi Pastinen, and Ossi Turunen Helsinki University of Technology, Finland, Hans E. Schoemaker DSM Research, The Netherlands
2. Hoekstra, Phillip – “Next Generation Technology for Enhancing Pulp Bleaching” – TAPPI PEERS 2016