Enzymatic Bleaching
Back From the Drawing Board

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Buckman
Chemistry, connected.
Let’s organize our thoughts…

- What are enzymes? (…and what enzymes are not)
- Wood fiber, wood chemistry and how enzymes fit in
- A brief history of enzymatic bleaching
- Current state of the technology
- The future
- Wrap up
What are enzymes?

- Enzymes are proteins with very specific chemical functions.
- They are typically naturally occurring chemicals employed by living systems for a myriad of functions – Our bodies use multiple enzymes throughout the digestive process as an example.
- Man probably first used enzymes in the manufacture of alcohol.
- Today enzymes are used in countless industries, and their manufacture represents over a US$8.1 Billion dollar a year business.
- Enzymatic modification of fiber in packaging and tissue production has been around for over 30 years.
What enzymes are not…

- Enzymes are the *chemicals* produced by living organisms; they are not in themselves living organisms.
- Enzymes do not multiply; they are finite.
- Enzymes do not adapt to conditions; they are not mutagenetic. If the conditions don’t match the capability of the chemistry, the chemistry doesn’t work.
- Enzymes are not indestructible. They can be deactivated and reactivated under certain conditions; they can be denatured (destroyed) under other conditions.
In wood, there are fibers, which are primarily cellulose, surrounded by lignin.

The bulk of the lignin is removed in the cooking process and the fibers are separated.

After cooking, fibers are still “coated” with a hemicellulose-lignin matrix.
Basic wood fiber and wood chemistry - bleaching

- Most of the remaining lignin and associated wood acids are attached to the fibers through a hemicellulose matrix.
- Conventional bleaching either oxidizes the lignin or breaks down the hemicellulose matrix releasing the lignin.
It’s all about selectivity

- Kraft cooking is not highly selective towards lignin but works well initially in the process because there is so much bulk lignin to begin with.

- Conventional bleaching agents are more selective towards lignin (and to some degree for hemicellulose) but they still will attack cellulose giving lower yield and lower strength, especially at the higher brightness.

- Enzymes are very specific towards breaking down hemicellulose. This allows lignin to be separated from the fiber without damaging the cellulose.
Bleaching enzymes – a very brief history

- The concept of commercial pulping/bleaching enzymes began in the late 1980s.
- The 1990s saw the end of chlorine bleaching and the advent of ECF bleaching and TCF bleaching to a lesser degree.
- Chlorine dioxide is expensive and the push was on for alternative methodologies.
- Oxygen delignification took us part of the way.
- Enzymes were seen as a potential next step.
Bleaching enzymes – the first generation

- The first generation worked, but conditions had to be perfect.
- The pH needed to be 6.5-7.0, retention times for 2 hours and temperatures under 60°C (140°F).
- Not many places in the pulp mill where these conditions exist naturally.
- The process had to be modified, pulp had to be acidified, and sulfuric acid was the chemical of choice.
- This proved to be “problematic” for several reasons.
- Most mills walked away.
15 years later and things have changed

- Next generation enzymatic technology offers us a new opportunity to reduce chlorine dioxide and the subsequent formation of AOX.
- This time, non altered conditions within a Brown High Density storage are acceptable in a lot of cases.
- Chlorine dioxide reductions as high as 20% have been obtained.
- Fiber quality and yield have not suffered as a result. We now have a pure xylanase product as compared to a blend with cellulases as was the case in the earlier generations.
Current process condition requirements for pre-bleach enzymes

- pH 5.5 – 10.0 (up to 10.2 in some cases)
- Temperatures between 40 and 90°C
- Chlorine residuals less than 20 ppm
- Residence time of at least 20 minutes
Current process condition requirements for post-bleach enzymes

- pH between 5.0 and 7.5
- Temperature between 45 and 80°C
- Chlorine residuals less than 20 ppm
- Retention time at least 30 minutes
Hardwood versus softwood

- Xylanases work best on Hardwoods, but will work on softwoods as well.
- Almost all hemicellulose present in hardwoods is in the form of xylans. It is a blend in softwoods.
Hemicellulose in softwoods

Source: Unknown
Hemicellulose in hardwoods

Source: Unknown
Let’s talk about advantages

- Lower bleaching chemical consumptions and cost
- Less ClO$_2$ means lower AOX formation
  - Lower effluent toxicity
- Depending upon configuration, the mill can reclaim organics to the recovery cycle through a prebleached washer (turning BOD into BTUs)
- Lower brightness reversion
- Lower “b” color values (pulp is less yellow)
...and address concerns

- **Yield**
  - Enzymes are very selective. While surface xylan removal is increased by using enzymes, they do not damage the cellulose.
  - In order to get equivalent brightness with conventional oxidative bleaching, we are sacrificing some of the cellulose to remove the same chromophore containing hemicellulose.
  - At equivalent brightness, net yield with enzymes should be about the same when compared to conventional bleaching.
Fiber strength characteristics

- Extensive lab and mill evaluations have proven that basic pulp characteristics after using pre- and post-bleaching enzymatic products are unchanged and possibly improved slightly.
- Because of the selectivity towards surface xylan, we are only impacting a very small portion of the fiber.
- Trials have been conducted and the paper has been traced out to the final user with respect to any adverse impact…
- …None has been found so far in the grades studied.
Typical beater curves on enzymatically treated hardwood

![Graph showing CSF and Tensile index (N m/g) for different treatments]
Beater curve data (continued)

**Burst index (KPa m²/g)**

- 100% ClO₂
- No enzyme
- 150 ppm BLX

- 0, 500, 1000, 1500, 2000

**Tear index (mN m²/g)**

- 100% ClO₂
- No enzyme
- 150 ppm BLX

- 0, 500, 1000, 1500, 2000
COD/BOD release

- We have seen an increase in COD content in the $D_0$ filtrate (or prebleached washer filtrate) of enzymatically treated pulps. This raises obvious concerns, especially if there is no prebleached washer returning filtrate back to the liquor cycle.

- COD sources are changed from chlorinated (oxidized) phenols to unchlorinated (unoxidized) phenols and xylose.

- These materials are much easier to treat in the wastewater treatment plant. Although influent COD loading will increase, the net effect in most commercial applications has been found to be neutral with respect to effluent BOD levels when given the chance to work through the wastewater treatment plant.

- Some mills have actually taken advantage of this to off load recovery boilers by raising kappa targets.
Pre-bleach vs. post-bleach?

- Very specific on what the mill is looking for

  **Pre-bleach**
  - Higher program cost but higher potential ROI
  - Opportunity to debottleneck (higher kappa)

  **Post-bleach**
  - Better impact on brightness reversion and pulp color
  - Alternative if brown stock pH conditions are not achievable
A 20% reduction in ClO$_2$ will correlate to a similar reduction in AOX formation.

Less chlorinated phenolics means a low overall effluent toxicity.

If the organics released by bleaching enzymes are not sent to the recovery cycle (higher BTU content) the sugars and lower chlorinated phenolics should mean an easier effluent to treat.
What will the next generations of enzymes look like?

- Expand the pH regime even further (11.0 would be nice, 12.5 would get us into pre $O_2$ delignification applications)
- Explore mechanisms to work on other forms of hemicelluloses (i.e., mannose, arabinose, etc.)
  - Leading to custom blends depending upon wood species
- Find and commercialize enzymatic technologies to break down wood extractives (pitch) that can be applied like pre-bleaching enzymes.
- Fast acting enzymes that can be applied to an incoming wood stream as a cooking aid.
Thank you for your time.

Questions?