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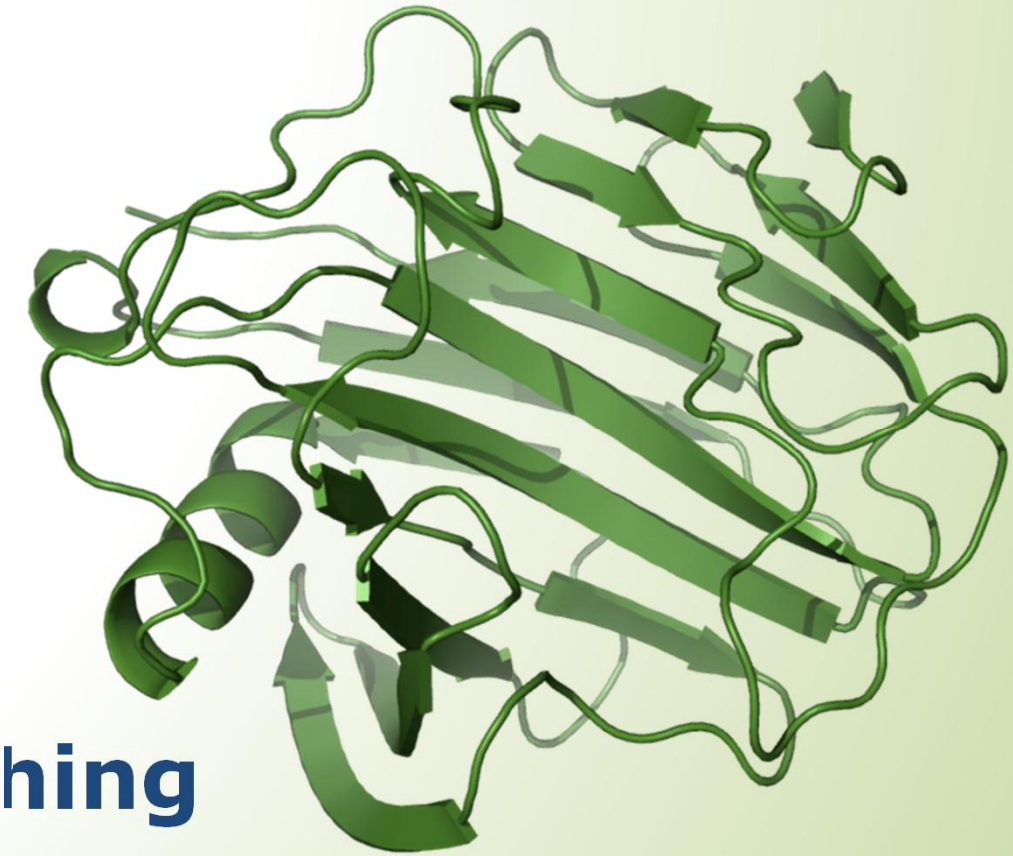


Enzymatic Bleaching

Sabrina Burkhardt
Pulping, Bleaching & Dissolving Supervisor
Econotech Services Ltd.

Agenda

- Enzyme basics
- Chemistry
- Brief history
- Enzyme types
- Going commercial
- Optimistic outlook

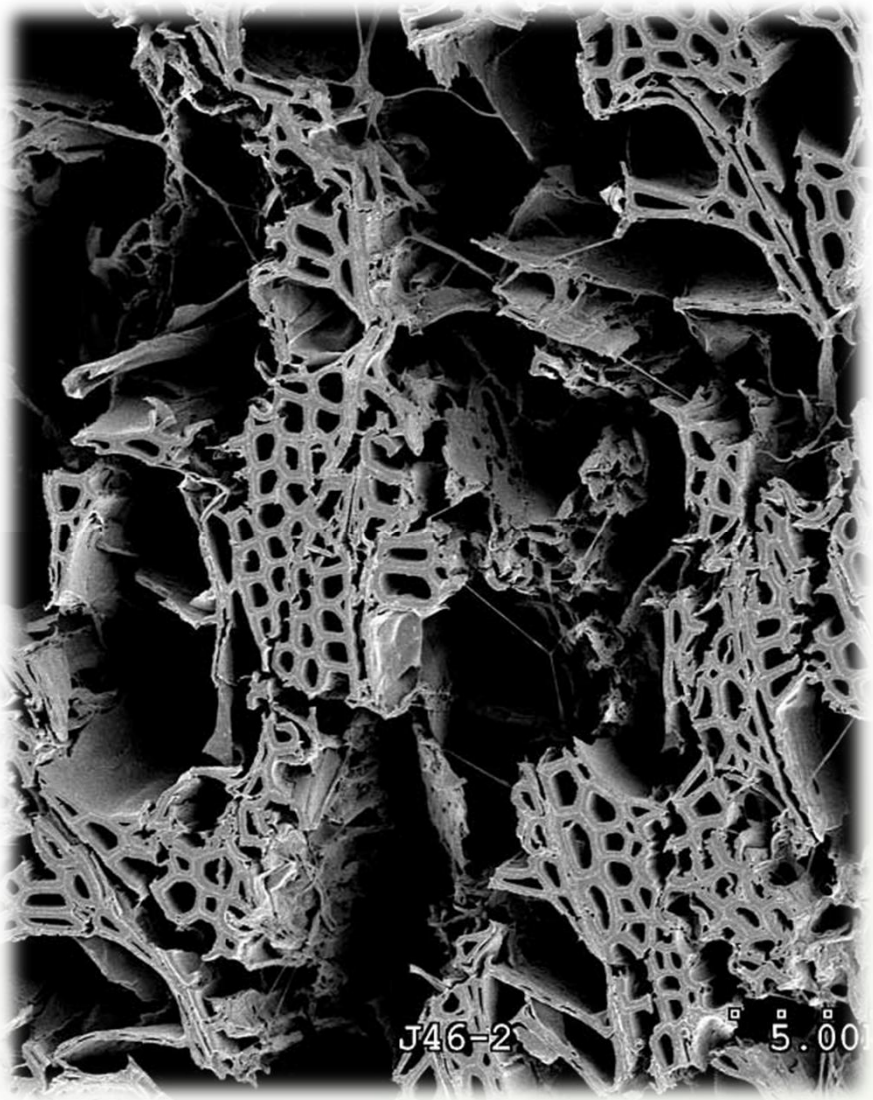
Enzymes – what are they?

- Proteins released from a variety of microorganisms – fungi, bacteria
- Biological catalysts to complete a specific task
- Have evolved in a wide range of environments – acidic/basic, hot/cold

Enzymes – what do they do?

- Everything from breaking down food to woody biomass
- Highly selective action
- Classifications we care about:
  - Oxidoreductases
  - Hydrolases

Enzymes for wood degradation



Extracted from wood-rot fungi, and other bacteria:

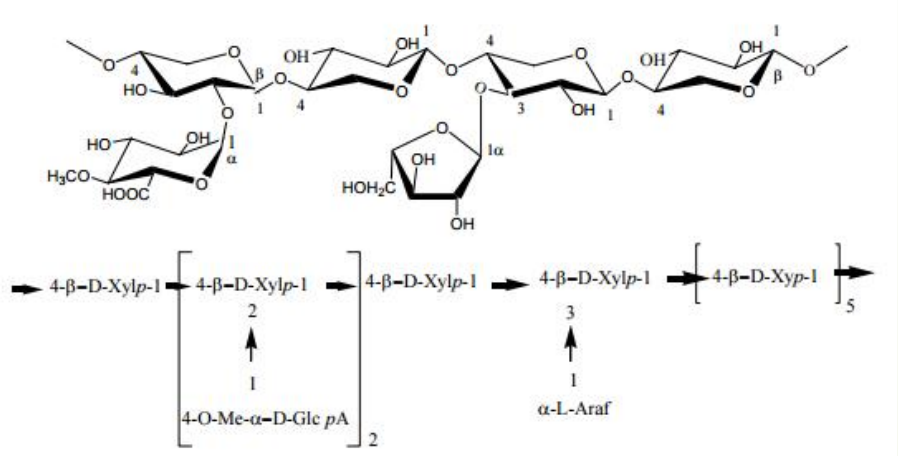
- Hydrolases:
  - Cellulases
  - Hemicellulases (xylanases, mannanases)
- Oxidoreductases:
  - Laccases
  - Peroxidaises

Photo Source: Robert A. Blanchette / Joel A. Jurgens, University of Minnesota, ecology.com

Wood Chemistry

Hardwoods

- Lignin: 16-25%
- Hemicellulose: ~30%
- Primary hemicellulose: glucuronoxylans (15-30% wood)



Softwoods

- Lignin: 23-33%
- Hemicellulose: ~27%
- Primary hemicellulose: galactoglucomannnan (10-15% wood)
- Secondary hemicellulose: arabinoglucuronoxylan (5-10%)

Photo Source: ipst.gatech.edu

After kraft pulping

High alkalinity and temperature leads to:

- Dissolution of much lignin, extractives, and majority of mannan hemicelluloses
- Xylan hemicelluloses often reprecipitate on fibers during cook (up to 15% of initial)
- Glucuronic acids for hexeneuronic acids and can bind to lignin

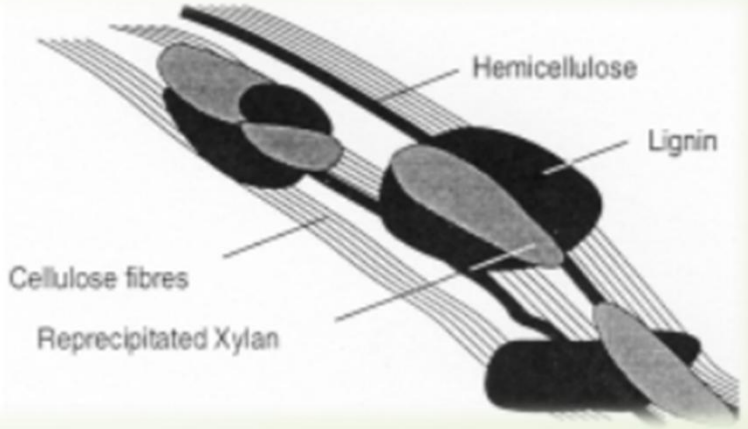
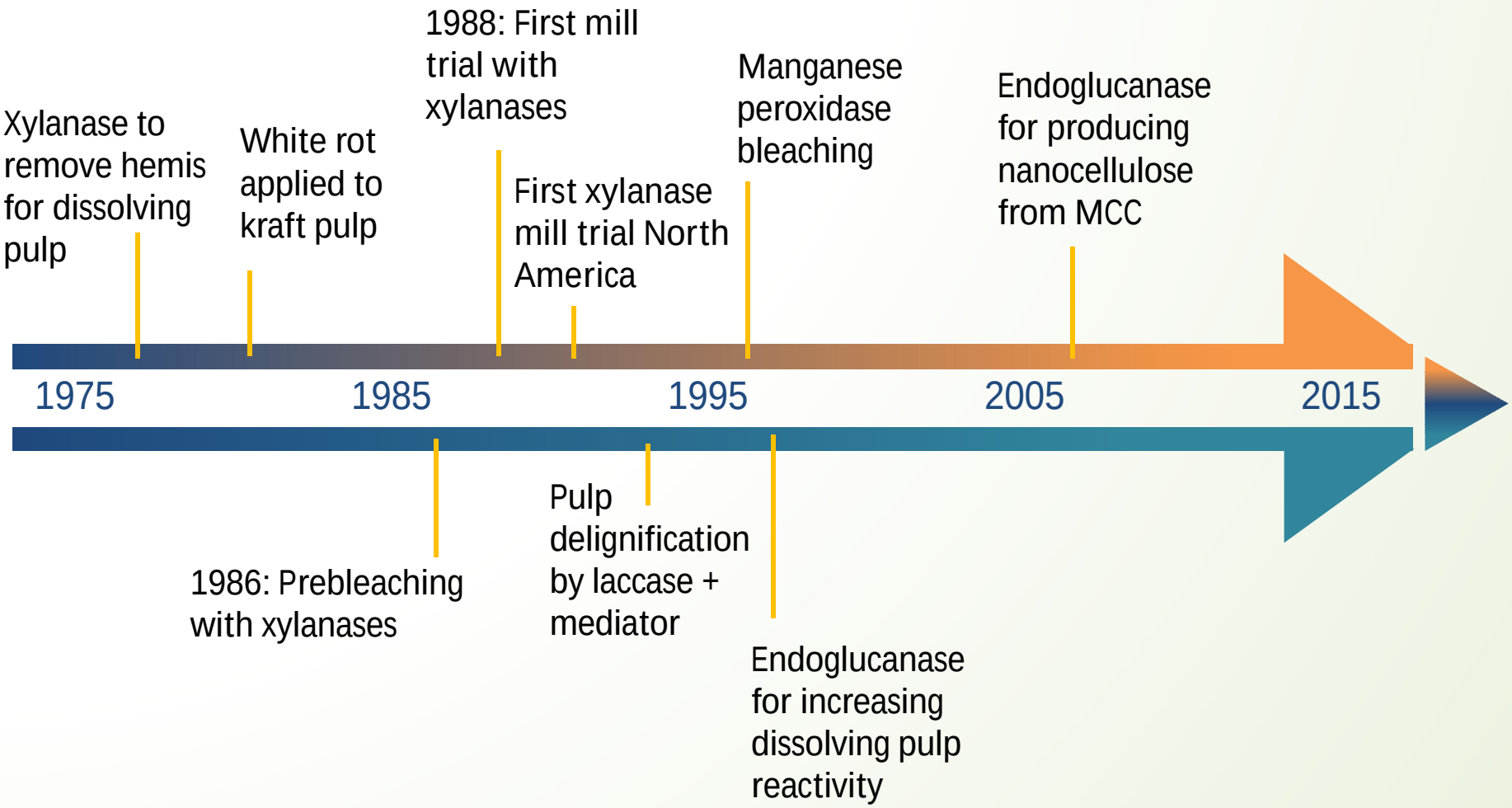


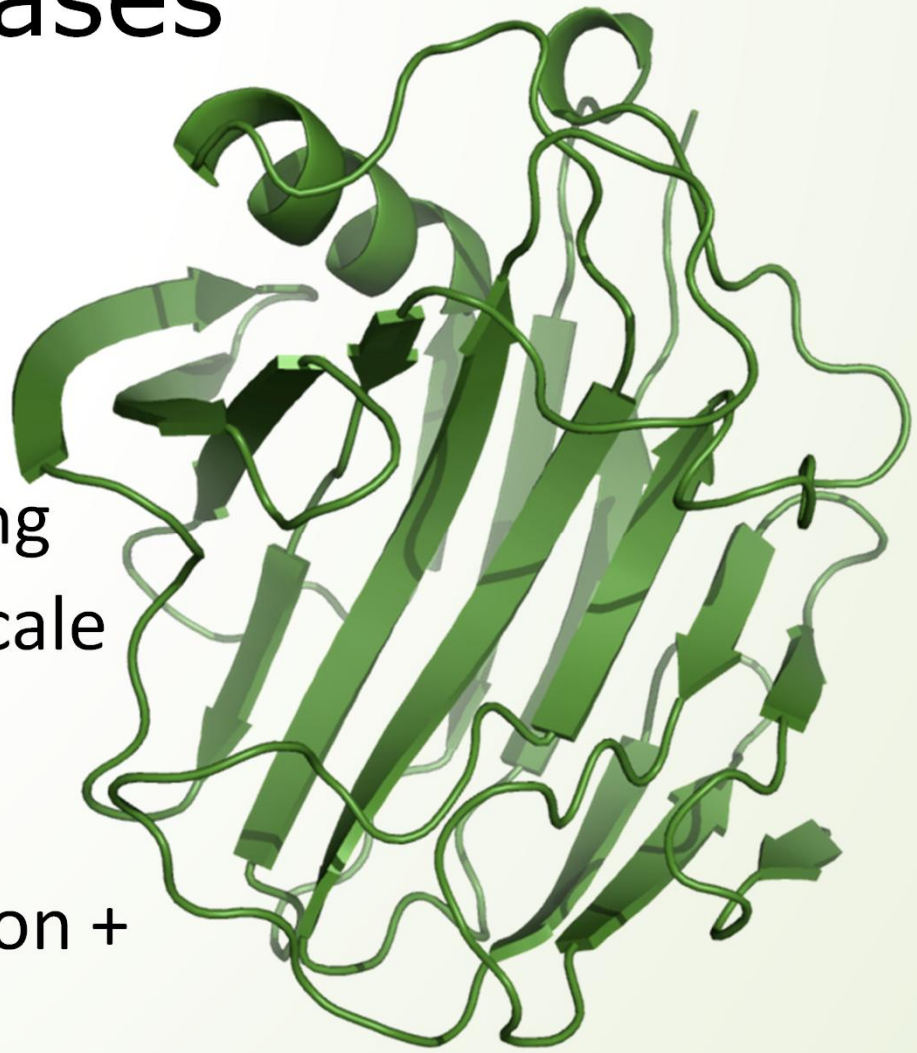
Photo Source: University of Auckland, School of Biological Sciences, Forestry – Dr. David Saul

History of enzyme use in Pulp Bleaching



Cellulases

- Endoglucanase
- Cellobiohydrolase

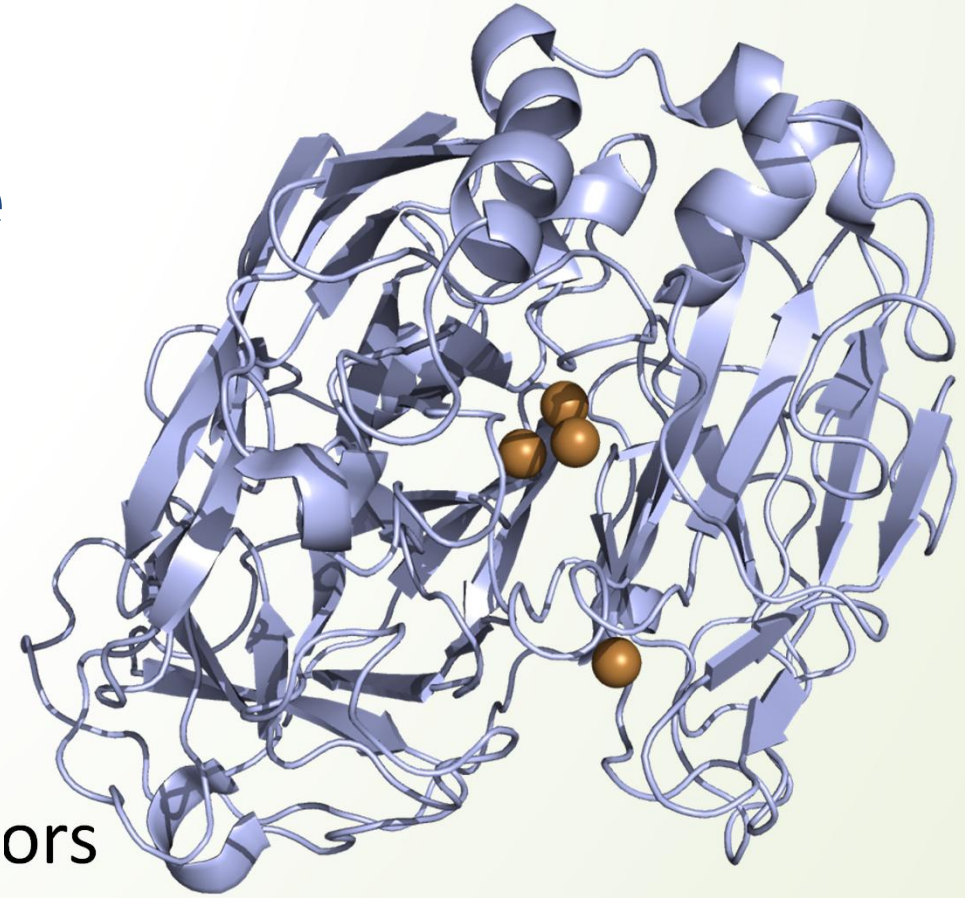


- Little use in pulp bleaching
- Have been used at mill-scale
- Causes reduction in viscosity/DP cellulose
- Good for fiber modification + deinking

Picture source: "1NLRribbon" by Nicholas Sawyer.

Lignin-oxidizing enzymes

- Laccase
- Manganese-peroxidase
- Lignin-peroxidase
- Derived from white rot fungi
- No trials at mill-scale
- Early attempts to use these enzymes failed
- Need mediators/ chelators to attack



Picture source: Armstrong research group, Oxford University

Lignin-oxidising enzymes

Advantages

- Attack lignin directly (no carbohydrate degradation)
- Can remove more lignin than an O_2 delig stage
- Shorter reaction time than white rot fungi (≤ 24h)

Limitations

- Requires mediators – which are expensive, toxic, and variable in performance
- Still needs relatively long contact time
- Much more research is needed to understand this system

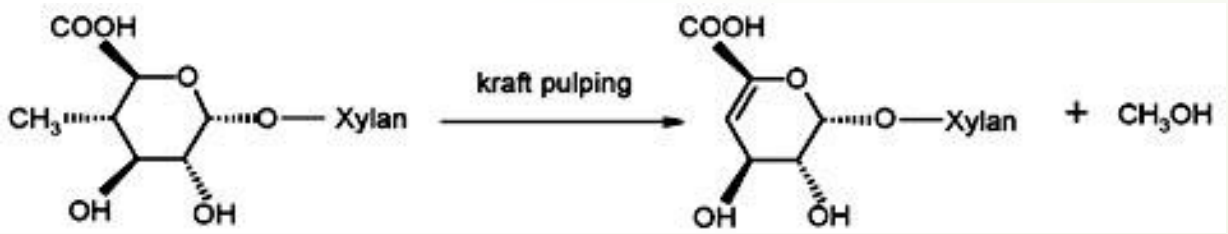
Hemicellulases

- Xylanase
- Mannanase
- Biggest success story
- Unexpected pulp brightening properties
- Xylanases more effective than mannanses on both HW & SW species
- Synergism reported when using both hemicellulases in some studies

Picture source: portalice.ca

Xylanase delignification – proposed mechanisms

- Hydrolyses reprecipitated xylan on the surface of fibers, allowing more lignin to diffuse
- When the xylan is cleaved, any monomers that are linked to lignin (LCC bonds), may also be liberated
- Xylanase also helps to release Hex-A, which has been shown to bond to lignin after pulping



(Formation of Hex-A during pulping) Source: Petit-Breuith et al 2004, J. Chilean Chem Soc.

Hemicellulases: advantages and limitations

Advantages

- Decrease in chlorine-chemical usage: ~20% for HW, 15% for SW
- Chemical cost savings
- Decrease in AOX in effluent
- Increased brightness ceilings
- Easy application to most bleaching processes

Limitations

- Strict temperature and pH control needed
- Corrosion issues reported at mill scale due to H_2SO_4 application to acidify brownstock pH

Challenges with commercial enzyme treatments

- pH
- Temperature
- Source of enzyme
- Wood species
- Quantity applied
- Contact time
- Cooking and bleaching chemistries/ conditions
- Lab-scale trials to fine tune all of the above

Accessibility to reaction sites is key!

Picture source: Vancouver Sun

Enzymes – an optimistic outlook

- Opportunity for mills to save on chemicals costs, simultaneously reducing environmental impact.
- Xylanases are available and have been running in mills for nearly 30 years
- Room for growth of enzyme use as pre-bleaching aid
- Expect more developments in these fields:
  - Laccases: potential to reduce kappa by 50-70%, but currently need an expensive/toxic mediator
  - Endoglucanase and xylanases: increased interest as a post-bleaching treatment

Questions?