

Project Title: Enhancing pulp properties of recycled fibers with oxidative enzymes

PROJECT OBJECTIVE:

Agenda 2020 has identified the need to improve the quality of recovered fiber. This project addresses this challenge with the use oxidative enzymes, such as laccase and soybean peroxidase/hydrogen peroxide, that increase the fiber charge of recycled fibers. By increasing the number of surface carboxylic acid groups on recycle fiber, this treatment will improve paper strength. In addition, oxidative enzyme treatments can also enhance brightness and color removal.

PROJECT BACKGROUND:

In 2005, a record 51.5 percent of the paper consumed in the U.S. (51.3 million tons) was recovered for recycling.¹ However, continued growth in exports of recovered paper and board to China has increased the cost and reduced the availability of secondary fiber.² The development of methods to improve paper strength and optical qualities would enable mills utilizing recycled fiber to shift to lower cost, lower quality grades while still maintaining product quality. Chemical oxidation of cellulose fibers to increase the number of fiber surface carboxylic acid groups has been shown to improve fiber strength properties.^{3,4} Enzymatic fiber oxidation with laccase has been reported to result in paper strength improvements^{5,6} thought to be due to the increase in fiber surface carboxylic acid groups.⁷ Preliminary work in Ragauskas' group has shown that treatment of recycled fibers with an oxidative enzyme such as laccase increases the surface carboxylic acid group content of recycled MOW (Figure 1) and resulted in improved paper strength properties (Figure 2).

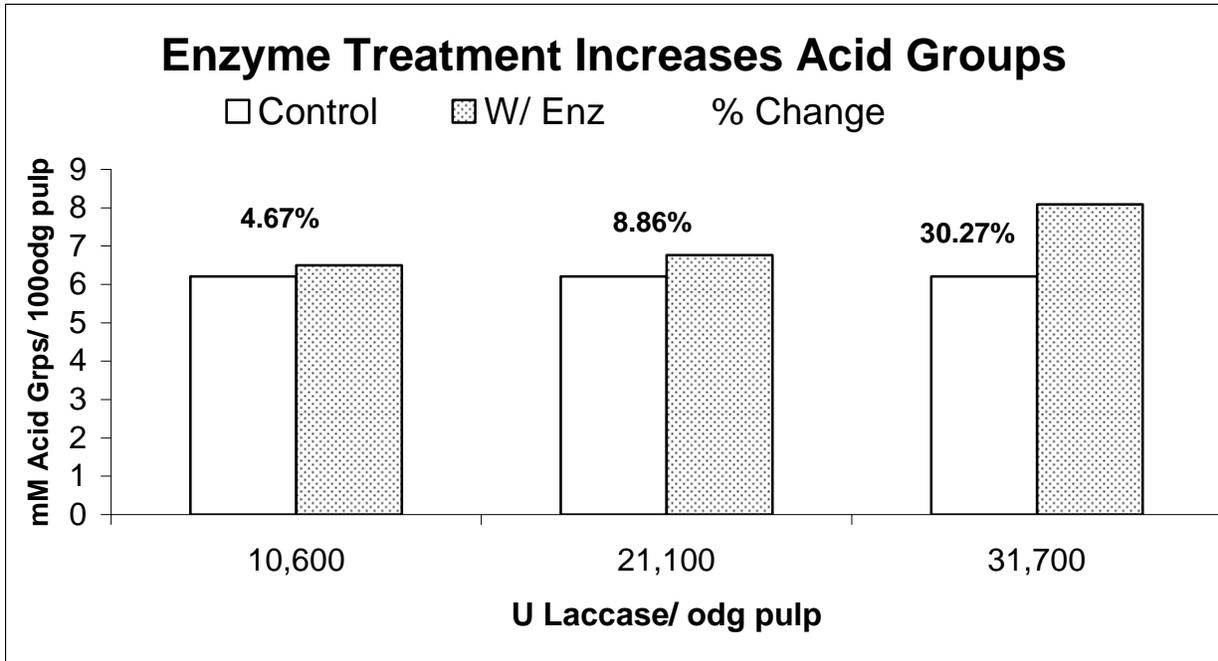


Figure 1 Laccase treatment providing increased fiber surface carboxylic acid group content of recycled fiber from a colored office paper

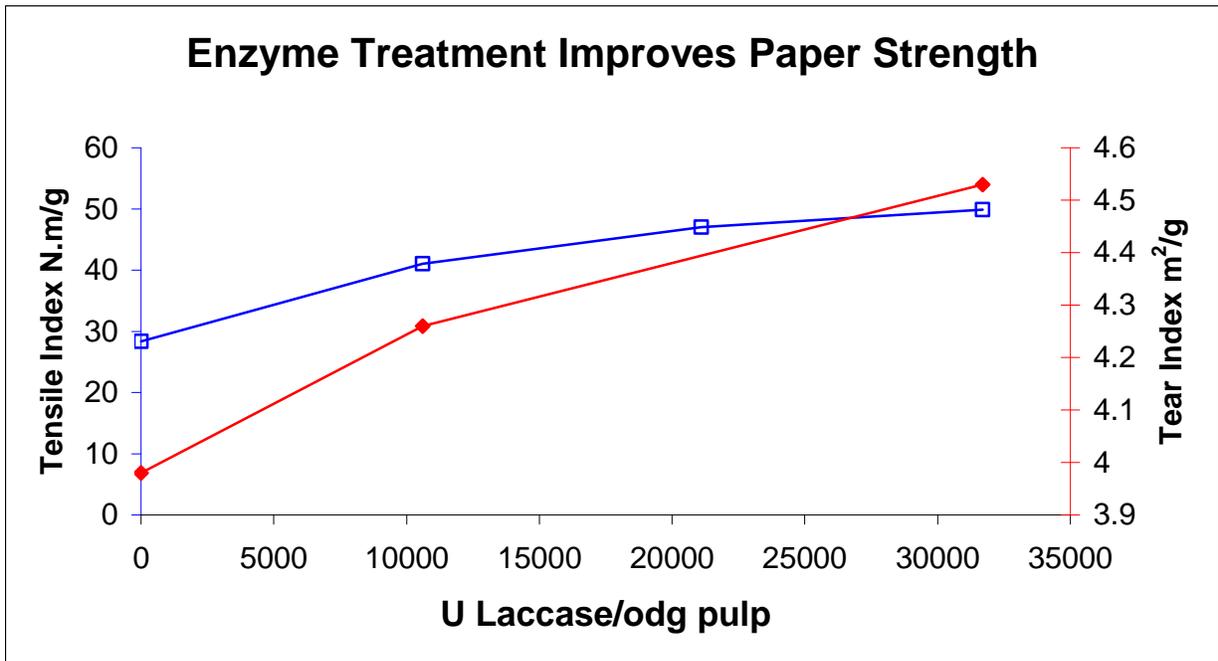


Figure 2 Laccase treatment improved tensile and tear strength of recycled fiber from a colored office paper

Laccases (EC 1.10.3.2) are oxidoreductases that combine single-electron oxidization of substrates with the reduction of oxygen to water.⁸ Peroxidase enzymes also oxidize substrates but obtain electrons from hydrogen peroxide rather than oxygen. Studies on biobleaching of virgin

pulp have focused on lignin and manganese peroxidases. However, soybean peroxidase (SBP), produced from the hulls of soybeans, is commercially available, inexpensive, and stable over a wide pH range (pH 3-8.5). (Figure 3)

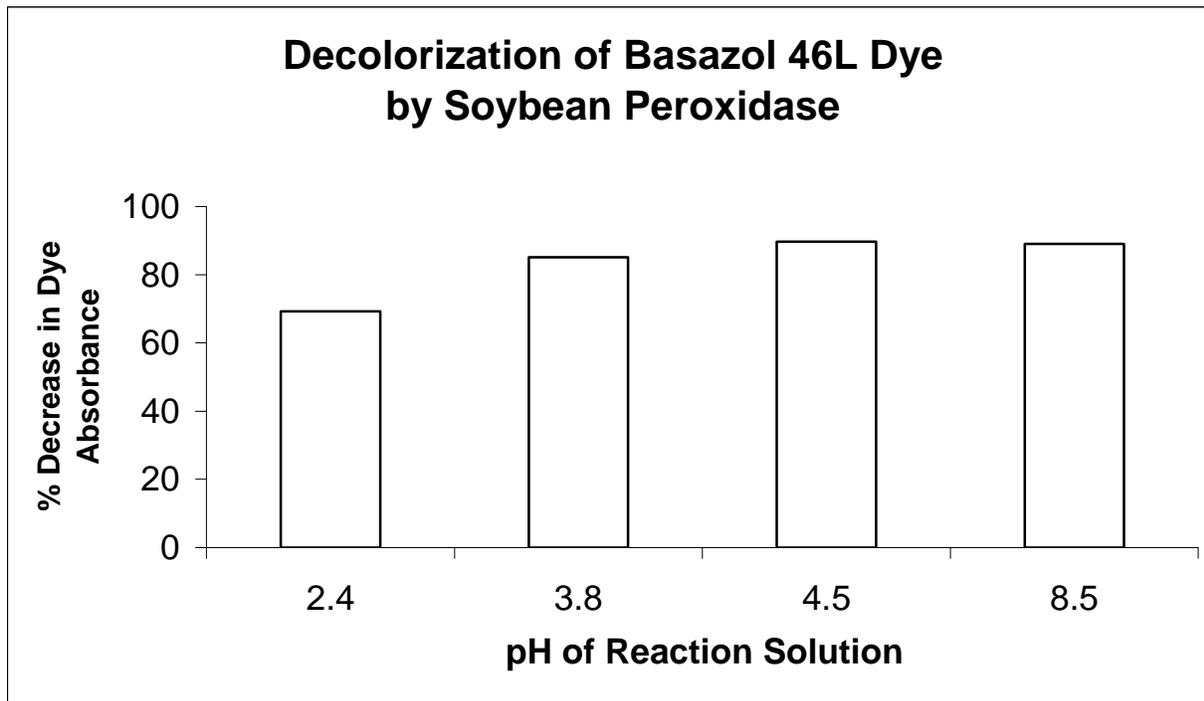


Figure 3 Soybean Peroxidase was able to decolorize a common paper dye over a wide range of reaction pHs¹⁰

One problem with utilizing recycled fiber from mixed office waste (MOW) is color due to dyes present in colored paper. Both laccase and soybean peroxidase have been shown to be effective in decolorizing two recalcitrant dyes commonly used in paper,^{9,10} in addition to facilitating bleaching of virgin pulps,¹¹ decolorizing mill effluents¹² and industrial dyes.¹³ Laccase has also been explored for use in deinking.¹⁴ This project would evaluate the potential for laccase and soybean Peroxidase/hydrogen peroxide treatment to improve strength and optical properties of recycled fibers from MOW.

PROJECT DELIVERABLES:

- ◆ Determination of the effect of enzyme treatments with laccase or soybean peroxidase on the number of fiber surface carboxylic acid groups, paper strength properties, brightness and color removal using commercial mixed office waste paper
- ◆ Comparison of effectiveness of enzyme treatment on MOW before and after deinking
- ◆ Evaluation of the most effective treatment point in the OY and PY bleaching sequences
- ◆ Optimization of the treatment conditions to achieve maximum improvement in strength and color removal
- ◆ Complete the technical report {June 2008}.

VALUE OF DELIVERABLES:

This program will provide an innovative technological package that can improve both paper strength and optical properties of secondary fiber. These results will allow recycled fiber mills to utilize lower cost lower quality furnishes, while still maintaining product quality.

PROJECT GOALS:

This program will evaluate the ability of oxidative enzymes (laccase and soybean peroxidase) to increase the number of fiber surface carboxylic acid groups, improve paper strength properties, increase brightness, and decrease color

PROJECT APPROACH:

Achieving the project goals requires completion of a number of stages that are summarized below.

I. Characterization of the properties of unbleached mixed office waste before and after deinking

- ◆ The first step in this project is to obtain and characterize unbleached mixed office waste before and after deinking
- ◆ Determine surface carboxylic acid group content of each pulp
- ◆ Measure tear and tensile index on handsheets
- ◆ Measure brightness and determine CIE L*a*b* color values

II. Investigation of the effect of deinking on subsequent enzyme treatment

- ◆ Treat repulped MOW and deinked MOW with laccase and with soybean peroxidase
- ◆ Measure surface carboxylic acid group content of treated pulps
- ◆ Measure physical and optical properties of handsheets from treated pulps
- ◆ Compare percentage changes in properties to determine whether enzyme treatments are more effective before or after deinking.
- ◆ Compare effectiveness of laccase treatment with soybean peroxidase treatment

III. Explore the ideal addition point in OY and PY bleaching sequences

- ◆ Enzyme treatment (T) will be performed as a separate additional step
- ◆ Subject the pulp to a three step bleaching sequence consisting of the various combinations:
 - Treatment before oxidation with oxygen (TOY) or hydrogen peroxide (TPY)
 - Treatment after reduction with dithionite (OYT and PYT)
 - Treatment between the oxidative and reductive stages (OTY and PTY)

IV. Optimize enzyme treatment conditions

- ◆ Determine ideal reaction time
- ◆ Test different reaction temperatures
- ◆ Test effectiveness at different pHs

References

1 Statistics compiled by American Forest and Paper Association, <http://stats.paperrecycles.org/>

² Lowney, Brendan Looking ahead PPI Pulp and Paper International Volume: (49)1, 19-21. (2007)

³ Barzyk, D.; Page, D. H.; Ragauskas, A. Carboxylic acid groups and fiber bonding. *Fundamentals of Papermaking Materials, Transactions of the Fundamental Research Symposium*, 11th, Cambridge, UK, Sept. 1997 (1997), 2 893-907; Le Roux, J.; Daneault, C.; Chabot, B. Acidic groups in TMP oxidized fibres by TEMPO to improve paper strength properties. *Pulp and Paper Canada*, v 107, n 4, p 39-41, April, 2006

4 Isogai, Akira; Saito, Tsuguyuki; Yoshida, Yutaka; Takihara, Tsuyoshi Chemical modifications of cellulose and cellulose derivatives. *Kinoshi Kenkyu Kaishi/Annals of the High Performance Paper Society*, Japan, n 44, p 35-42, 2005 L

⁵ Mansfield, Shawn D. Laccase impregnation during mechanical pulp processing - Improved refining efficiency and sheet strength. *Appita Journal*, v 55, n 1, p 49-53, January, 2002

⁶ Pei, Ji-Cheng; Shi, Shu-Lan; Wei, Hua-Li; Zhao, Wen-Bo; Ma, Li-Na Strength properties enhancement of unbleached kraft pulp through laccase catalyzed oxidation. *Chung-kuo Tsao Chih/China Pulp and Paper*, v 24, n 6, p 1-4, June, 2005

⁷ Chandra, Richard P.; Ragauskas, Arthur J. Modification of high-lignin kraft pulps with laccase. Part 2. Xylanase-enhanced strength benefits. *Biotechnology Progress*, v 21, n 4, p 1302-1306, July/August, 2005

⁸ Reinhammar, B. Laccase in copper proteins and copper enzymes, vol. 3. R. Lontie, Ed. (CRC Press, Boca Raton, FL. 1984) pp. 1-35

⁹ Knutson, Kristina, Ragauskas, Arthur. An Auspicious Application of Laccase and Hydrogen Peroxidases for Biobleaching of Recalcitrant Paper Dyes. *Proceedings International Society of Wood Pulping and Chemistry*, Madison WI, June 2003.

¹⁰ Knutson Kristina; Ragauskas Arthur Laccase-mediator biobleaching applied to a direct yellow dyed paper. *Biotechnology progress* (2004), 20(6), 1893-6.

11 Potthast, A.; Wittmann, E.; Fischer, K. Biobleaching of Pulp by Enzymes. *Fourth European Workshop on Lignocellulosics and Pulp: Advances in Characterization and*

Processing of Wood, Nonwoody, and Secondary Fibers, 162-164, (1996)

Conference: European Workshop on Lignocellulosics and Pulp: Advances in Characterization and Processing of Wood, Non-Woody and Secondary Fibers, September 8-11, 1996, Stresa , Italy

¹² Goncalves, M. Luisa F.C.; Steiner, W. Use of laccase for bleaching of pulps and treatment of effluents. *ACS Symposium Series*, 197-206, (1996) Proceedings of the 1996 211th National Meeting of the American Chemical Society, Mar 24-28 1996, New Orleans , LA , USA

¹³ Lonergan, Greg T.; Baker, W. L.; Schliephake, Kirsten. Detoxification and degradation of toxic industrial compounds and industrial dyes by white-rot fungi. An expanded role for laccase *Current Topics in Analytical Chemistry* (2004), 4 67-91

¹⁴ Xu, Qing-Hua; Qin, Meng-Hua; Shi, Shu-Lan; Zhang, Ai-Ping; Xu, Qian Synergistic deinking of ONP by cellulase/hemicellulase combined with laccase-mediator system. *Chung-kuo Tsao Chih/China Pulp and Paper*, v 23, n 8, p 6-9, August, 2004