Exploring the hypothesis that limiting diffusion of fungal oxidants underlies decay resistance in acetylated wood

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The mechanisms by which chemical modifications, specifically acetylation, improve the decay resistance of wood are a topic of active research. In the early stages of decay, fungi secrete low-molecular-weight oxidants or oxidant precursors. These oxidants diffuse through the wet wood cell wall and oxidize cell wall polymers, which enable the decay process to proceed. One hypothesis states that acetylation stops decay by dramatically inhibiting the diffusion of these oxidants through the cell wall (Zeiinka *et. al.* 2016). Data showing a drastic difference in Fe uptake from solution between control and acetylated wood appear to support this (Hoseinipour and Mai 2016).

It has been proposed that carbohydrate-rich domains in the cell wall (hemicellulose and non-crystalline cellulose) go through a glassy-rubbery transition upon water swelling and become the medium for ion transport (Jakes *et. al.* 2013, Zelinka *et. al.* 2016). Bulking treatments that reduce the free volume are hypothesized to prevent the carbohydrates from entering the rubbery phase, thus dramatically limiting diffusion inside the cell wall.

Figure 1 shows ICP measured Fe(III) uptake with ICP in pre-wetted loblolly pine wood acetylated to 0, 10, and 20 WPG after exposure to a large excess of solution mimickingthe conditions of fungal brown rot: 5 mM oxalate, 0.1 mM Fe(lll), and pH 3.9, with $Fe(lll) \cdot (oxalate)_3^{3-}$ as the dominant iron species. Fe uptake was measured between 1 and 79 hours of exposure. 10 samples, 2 mm longitudinal and weighing ~2 g, were removed at each time point, weighed wet, weighed dry, and then analysed for Fe content. Our original hypothesis predicted that acetylated wood would take up Fe(III) at a far lower rate and saturate at a lower concentration than control wood.

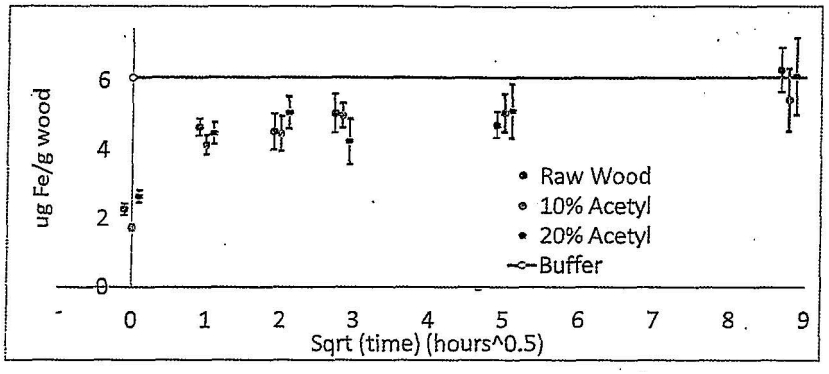

Figure1: Fe content of pine wood by ICP after various times soaking in 6 µg Fe/g oxalate buffer. Error bars represemt 95% confidence interval. 79 hour data is statistically different ($p<0.005$) from

Using 5mM oxalate buffer, we observed that both control and acetylated wood contained the same amount of iron after79 hours of soaking: 1.4x the solution concentration. The fact that pore volume was halved by acetylation to 20%, but carboxylate [COO^-] in wood is unchanged suggests that the amount of Fe observed in the wood was determined by the ability of wood COO^- to compete with the very strongly chelating oxalate buffer for Fe. We conclude that the similar experiments of Hosseinipour and Mai (2016), where the wood adsorbed and retained 3180x as much Fe per ml as the surrounding solution, reflect the ability of wood COO^- and hydroxyl groups to compete effectively for Fe against their acetate buffer. Since acetylation interfered with Fe uptake from acetate buffer, it appears likely that OH groups have a role in Fe chelation when oxalate is absent.

In our experiments, diffusion was largely complete by the first data point, 1 hour. A full diffusion model must be run to establish the lowest diffusion rate of Fe(III) in acetylated wood consistent with the data.

References

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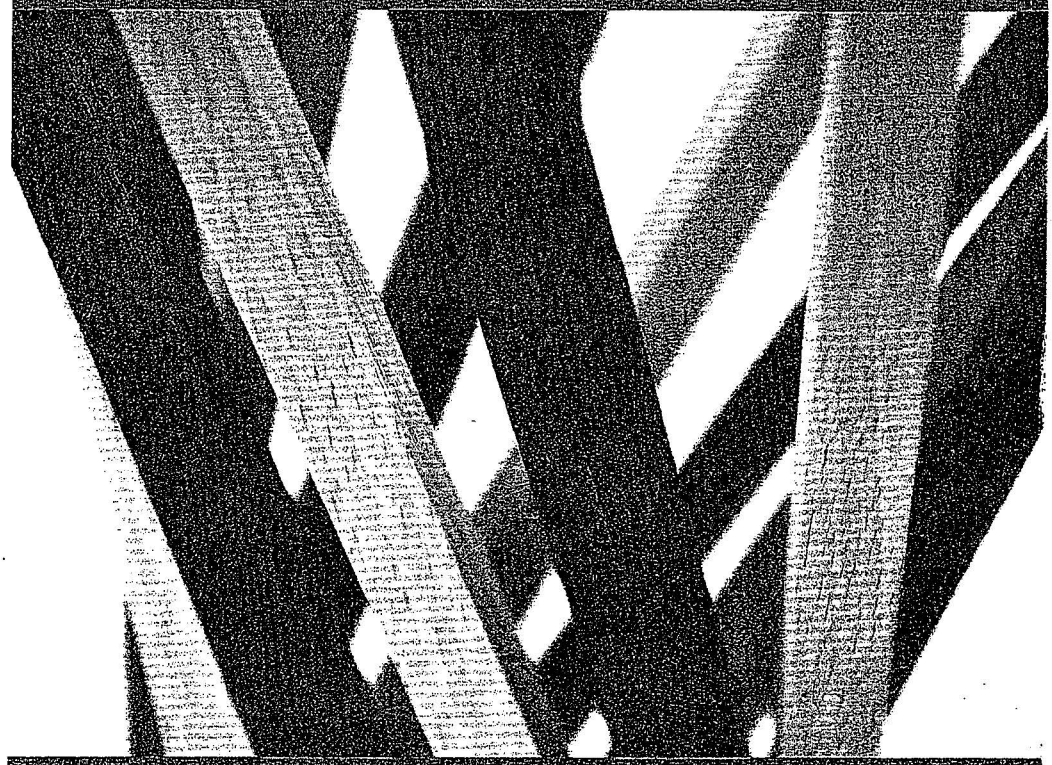

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