

## IMPREGNATION OF BIO-OIL FROM SMALL DIAMETER PINE INTO WOOD FOR MOISTURE RESISTANCE

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Wood pyrolysis oil consists of hundreds of complex compounds, many of which are phenolic-based and exhibit hydrophobic properties. Southern yellow pine was impregnated with a pyrolysis oil-based penetrant using both a high pressure and vacuum impregnation systems, with no significant differences in retention levels. Penetrant concentrations ranging from 5-50% pyrolysis oil/methanol on a volume basis were used to determine the threshold concentration for significant physical property improvement. Wood impregnated with penetrant concentration of at least 10% exhibited significant reduction in both moisture sorption and tangential swelling when exposed to a 90% relative humidity and 21°C environment. When exposed to liquid water in a 24-hour soak test, analysis revealed a negative linear relationship between penetrant concentration and both moisture sorption and tangential swell. However, during the course of the 24-hour soak test, a significant linear relationship between penetrant concentration and leachate was determined.

*Keywords:* Bio-oil; Pyrolysis oil; Pressure treatment; Moisture resistance; Southern yellow pine

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### INTRODUCTION

In the southeastern United States, southern pine is the dominant resource for the production of lumber, railroad ties, telephone poles, and other commodity forest products. Products made from southern pine typically exhibit lower dimensional stability when compared to similar products made from other sawtimber species such as aspen. This negative attribute is primarily a result of the increased juvenile wood concentration and high microfibril angles exhibited by southern pine originating from plantations where fast-growth and early harvest are considered operational priorities (Via et al. 2009). For example, longleaf pine juvenile (*Pinus palustris*) grown in a dense plantation environment exhibits microfibril angles as high as 55° within individual growth rings (Via et al. 2007). Shupe and colleagues (1996) reported average microfibril angles as high as 43° for loblolly pine (*Pinus taeda*), a primary source of sawtimber within the southeastern United States. High microfibril angles translate into high longitudinal shrinkage or swelling; resulting in product warp, twist, or cupping.

Altering the product to resist moisture absorbance by filling wood lumens with a hydrophilic material is the most direct way of reducing the severity of swelling,

regardless of the percentage of juvenile wood within the timber product (Furuno and Goto 1978). Extensive research has been conducted on cell wall bulking agents over the past 30 years, resulting in a considerable literature base. Three primary classifications were developed to describe the interaction of cell wall bulking agents within the wood microstructure. These classifications are based upon the bonding efficiency and leachability of the bulking agent to and from the wood substrate (Wallström and Lindberg 1999). The first classes of impregnable chemicals are termed nonbonded-nonleachable (NBNL) treatments, such as phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins. These chemicals are reactive polymers that impregnate and then react to form a solid, non-leachable polymeric material within the wood cell lumen. Research focusing upon these interactions has failed to provide conclusive proof of covalent bonding to the cell wall (Gabrielli and Kamke 2010). The second type of impregnate is comprised of nonbonded-leachable (NBL) compounds. These products are represented by materials such as polyethylene glycol (PEG), which impregnate within the wood structure, yet provide no cell wall interaction and little resistance to leaching from free water entering and leaving the wood substrate. These chemicals are used primarily in the wood products industry as a means to reduce shrinkage and cracking in artistic and furniture grade lumber products. The final impregnable chemical type consists of bonded-nonleachable chemicals (BNL), such as epoxies and isocyanates which impregnate and form covalent bonds with the cell walls of the wood substrate, imparting long-term moisture resistance during cyclic changes of environmental moisture (Rowel and Ellis 1978). These impregnates produce a superior wood-polymer composite; however, the cost incurred during the production of epoxy/isocyanate wood composites restrict their use to extreme high-end applications.

For decades, it has been known that lignin produced from various pulping processes could be utilized as a filler to impart hydrophobic properties to lignocellulosic materials. The high concentration of phenolic compounds within the molecular structure of lignin provide a naturally moisture resistant feedstock (Goring and Rezanowich 1958). The cellulose and hemicellulose constituents of wood are considered hydrophilic, and thus they are responsible for a significant portion of moisture sorption in wood due to the affinity of water for the hydroxyl functional groups within the cellulosic polymer subunit (Bjork and Rasmuson 1995). Finding ways to incorporate phenolics from under-utilized lignin sources in an effort to lower the moisture sorption of wood products naturally high in cellulose and hemicellulose would provide an environmentally sustainable and economically beneficial value-added product.

Wood pyrolysis oil is a product rich in phenolic compounds, providing a possible solution to the current dependence of the wood products industry on petroleum-based phenolic compounds. The cost of pyrolysis oil has recently been shown to be 3 times less than the price of an equivalent volume of gasoline and is thus considered to be a potentially cost-competitive value added chemical (Badger et al 2011). Impregnation of wood pyrolysis oil into solid wood products will provide a cost-effective alternative to conventional treatment options utilizing petroleum-based products. After bio-oil synthesis, the refined product could be impregnated into solid wood products using methods synonymous to conventional wood preservation. The high concentrations of

phenolic, hydrophobic compounds in wood pyrolysis oil offer a viable solution to the current coal and petroleum-based industrial treatment options.

Production of bio-oil requires the fast pyrolysis of lignocellulosic feedstock, whereby feedstock is introduced into a chamber whose temperatures are increased rapidly to the range 400 to 500 °C, with vapors rapidly quenched by condensation, thus producing a highly reactive product in chemical dis-equilibrium (Mohan *et al.* 2006). The resulting pyrolysis bio-oil consists of a combination of both high and low molecular weight compounds, phenols, organic acids, and guaiacols (Hilton and Das 2010). Pyrolysis oils consisting of high concentrations of low molecular weight compounds are capable of penetrating cell lumens and pits within the cell wall. Regardless of molecular weight, a solvent is needed to reduce the viscosity and transport the bio-oil within the wood structure. Methanol is a common solvent for phenolic compounds and it also provides a means to methylate the bio-oil, thus reducing the rate of degradation over time (Hilten and Das 2010; Sakai *et al.* 1999). The mechanism for the ability of methanol to stabilize pyrolysis oil is complex and uncertain but is theorized and has been reviewed in Hilten and Das (2010). In addition, the fractionation of bio-oil into insoluble lignin-rich streams is not necessary prior to impregnation, resulting in reduced production costs for manufacturers (Mohan *et al.* 2008). This environmentally-friendly, moisture resistant treatment produces a biocomposite requiring fewer petroleum-based resources, with increased resistance to biological degradation, while utilizing a feedstock that originates from previously unmarketable, small diameter pine that is currently too expensive to remove from currently harvested sites (Bergman *et al.* 2010; Mohanty *et al.* 2001; Mohanty *et al.* 2000).

The objective of this research was to determine the feasibility of pressure-treating southern pine with bio-oil for improved moisture resistance. Retention values for southern pine, treated using both high-pressure impregnation and a vacuum impregnation techniques, were investigated. The minimum retention levels required for moisture sorption reduction were determined and tests of moisture sorption were conducted using both environmental chambers and submersion tests. Imaging analysis was performed to determine the distribution of bio-oil within the cell lumens and elucidate the mechanics of penetration.

## **METHODS AND MATERIALS**

### **Bio-oil Preparation**

Bio-oil was produced in an auger-style reactor, with controlled retention times and pyrolysis temperatures. Bio-oil used for treatments was a combination of oils produced at temperatures ranging from 425 to 500°C. The reactor utilized two condensers, the first without temperature control and the second maintained at 0°C to collect and condense aerosols and vapors. Each pyrolysis run utilized 500g of juvenile pine, and the condensate from each was combined to produce the total yield of pyrolysis oil.

The bio-oil was stabilized and homogenized by diluting the whole bio-oil to a 50% v/v concentration-using methanol. Methanol provides for methalization of the bio-

oil, preventing increases in molecular weight and degradation of the volatile components (Mohan *et al.* 2006). The diluted bio-oil was vacuum filtered five times to remove the char and particulate components using Whatman #2 filter paper. Filtration was vital for impregnation to prevent the clogging of vascular tissue within the wood structure. The initially diluted bio-oil was then further diluted using additional methanol to final bio-oil concentrations of 5, 10, 20, 30, 40, and 50% v/v.

### Pressure Treating

Southern pine (*Pinus spp.*) was cut into blocks (18×18×18 mm) from one board to avoid tree to tree variation. Before pressure treating, the blocks were conditioned to reduce moisture content (2.64±0.11 %) in a 60°C oven for 96 hrs before initial mass measurements. To facilitate retention calculations, individual blocks were numbered using steel stamps, and the mass was recorded. Then pressure treating was conducted using two techniques to elucidate differences in retention levels between high pressure impregnation and vacuum impregnation (detailed methods can be found in the next section). Retention was calculated using the following formula (AWPA E10-09),

$$R = (GC/V)*10 \quad (1)$$

where  $R$  is the retention of pyrolysis oil, kg/m<sup>3</sup>,  $G$  is  $(T_2-T_1)$ , the grams of treating solution absorbed by the block (difference in weight of block after treatment and before treatment),  $C$  is grams of bio-oil in 100 g of treating solution, and  $V$  is the volume of block in cubic centimeters.

### High Pressure Impregnation

Impregnation was completed using a pressure treatment vessel developed and constructed by the authors (Fig. 1). Using a Bethel full-cell process, wood blocks were placed within the vessel, and a vacuum of 27" Hg was achieved for a period of 1 hr. The treatment solution was then drawn into the vessel under vacuum. The vacuum was released, and compressed air (125 psi) was then maintained for a period of 1 hr. Upon completion, the vessel was opened, drained of solution and blocks were allowed to bleed excess treatment and air dry for a period of 24 hrs. After air drying, the blocks were again placed in a 60°C oven for a period of 48 hrs to allow for the evaporation of residual methanol. Mass measurements were recorded for each individual block to determine retention levels.

### Low Pressure Impregnation

Impregnation was completed using a vacuum oven (Thermo Electron Corporation Vacutherm). Wood blocks were placed in open-top containers and weighted to maintain submergence. Containers were filled with bio-oil solutions and placed under vacuum (27" Hg) for a period of 1 hr. The vacuum was then released, and the containers were allowed to rest at atmospheric pressure (*low pressure*) for a period of 1 hr. The containers were then drained and blocks were allowed to air dry for a period of 24 hrs. Residual drying was conducted as stated for high pressure treatment. No residual bleeding of excess treatment was observed in the low pressure process.



Fig. 1. Custom bench-scale vessel for *high pressure* treatment

### Moisture Sorption

Ten treated blocks and controls were dried to a moisture content of  $2.64 \pm 0.11\%$  in a  $60^\circ\text{C}$  oven for 96 hrs prior to moisture sorption analysis. Blocks were placed in a miniature environmental chamber (model 9140 PGC, Inc.) at 90% relative humidity and  $21^\circ\text{C}$ . Mass (0.0001g) and tangential swelling were recorded every 4 hrs for a period of 24 hrs. Tangential swelling was measured using a micrometer (Mitutoyo<sup>®</sup> Absolute indicator micrometer: 0.01mm). To measure moisture increase and tangential swelling in a water submergence situation, individual blocks were weighted and submerged at atmospheric pressure for a period of 24 hrs. A tangential swelling coefficient and swelling reduction efficiency measure were calculated using the following formulas modified from Rowell and Ellis (1978),

$$S = (T_2 - T_1) / T_1 \quad (2)$$

where  $S$  is the tangential swelling coefficient,  $T_2$  is the tangential length after wetting, and  $T_1$  is the tangential length before wetting. Also,

$$R = (S_2 - S_1) / S_1 \quad (3)$$

where  $R$  is the reduction in swelling resulting from treatment,  $S_2$  is the treated tangential swelling coefficient, and  $S_1$  is the untreated tangential swelling coefficient.

### Leach Analysis

Five treated blocks of each penetrant concentration were soaked in 200 mL of distilled water for 24 hrs at 20°C in normal atmospheric pressure. Leachate samples were collected and placed in a dark 4°C environment until analysis was conducted. Samples were diluted 10x prior to analysis. Spectrophotometric absorbance analysis was conducted using a ThermoScientific® Genesys UV scanning spectrophotometer. Absorbance values were recorded at 205 nm, which is the peak UV absorbance of lignin and aromatic rings that may be present in pyrolysis oil (Parasuraman et al. 2007).

### Hyper-spectral Imaging

To determine the distribution of wood pyrolysis oil within the wood microstructure, treated blocks were vacuum-soaked in distilled water for a period of 1 hr and microtomed (American Optical Company model 860) to a thickness of 150 microns. Microtomed sections were then placed on slides, immersed in glycerin and cover slipped. Imaging was performed using an Olympus BX41 Microscope equipped with a CytoViva hyperspectral imaging system v1.1 at 40× total magnification. Bio-oil was mapped within the cellular structure based upon spectral reflectance references using ENVI 4.4 imaging software.

## RESULTS AND DISCUSSION

Pyrolysis oil was impregnated using both the high pressure and vacuum systems at a concentration of 10% v/v and 50% v/v to determine whether retention values would vary. The pyrolysis oil was impregnated into the solid wood substrate with no significant difference or interaction effect in the retention levels between high pressure and vacuum impregnation (*two-way tests*: LP- 10%: 0.40±0.003, 50%: 4.48±0.15; HP- 10%: 0.44±0.006, 50%: 4.40±0.67 kg/m<sup>3</sup>, Fig. 2). The reason for the lack of difference between the low and high pressure treatment could possibly be due to the high surface area of the samples that were occupied by the transverse section of the wood. This allowed for easy penetration of the pyrolysis oil/methanol mixture into the wood. This is an important observation since lumber products have a different length to width ratio, which could result in a slower rate of penetration into the wood. Future research on large-scale samples would thus be useful.

Due to the reduced volume of penetrant necessary for treatment, safety and ease of using a low-pressure system, further treatments were conducted using low pressure, and all tests utilized low-pressure impregnated samples.

In an industrial setting, using the least amount of bio-oil treatment possible while still providing moisture resistance will maximize economic returns and minimize environmental impact. To determine this treatment threshold for increased moisture resistance, the samples were treated with dilutions ranging from 5 to 50%. The change in mass, or increase in moisture content, when exposed to water vapor became significant

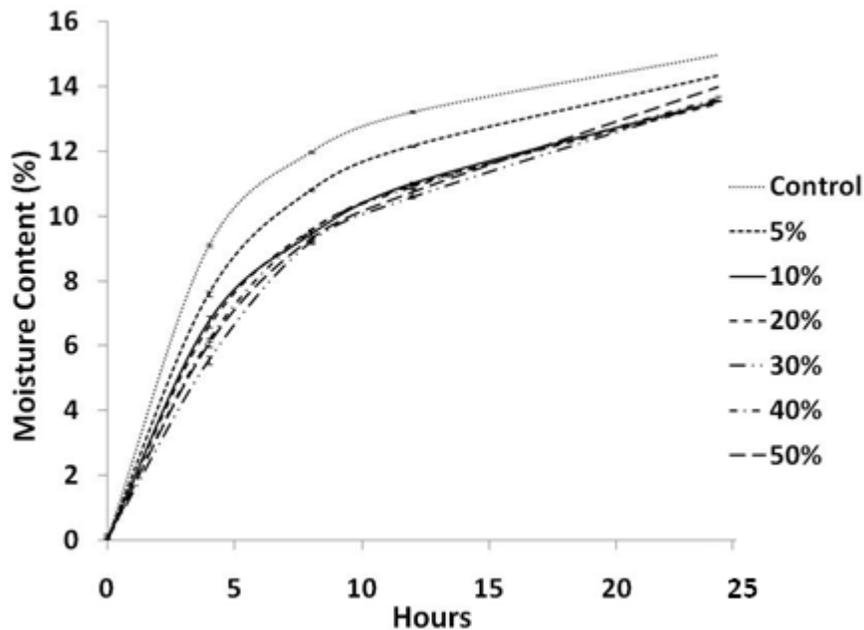
after 4 hrs of exposure. As illustrated in Table 1 and Fig. 2, a bio-oil concentration as low as 5% provided significant moisture resistance when compared to control; however, there was no further significant increase in moisture resistance in concentrations above 10%.

**Table 1.** The Mean Change in Tangential Expansion (%) and Mass Change (%) to Pyrolysis Oil Concentration  $\pm$  Standard Deviation \*

Hour	Pyrolysis Oil Conc (%)	Mass Change	Tangential Change
4	0	9.10 $\pm$ 0.28 <sup>A</sup>	2.03 $\pm$ 0.31 <sup>A</sup>
	5	7.61 $\pm$ 0.57 <sup>B</sup>	1.91 $\pm$ 0.21 <sup>AB</sup>
	10	6.74 $\pm$ 0.42 <sup>C</sup>	1.66 $\pm$ 0.13 <sup>ABC</sup>
	20	6.58 $\pm$ 0.39 <sup>C</sup>	1.51 $\pm$ 0.25 <sup>BCD</sup>
	30	5.55 $\pm$ 0.26 <sup>D</sup>	1.46 $\pm$ 0.34 <sup>BCD</sup>
	40	6.17 $\pm$ 0.15 <sup>CD</sup>	1.40 $\pm$ 0.17 <sup>CD</sup>
	50	6.04 $\pm$ 0.25 <sup>CD</sup>	1.06 $\pm$ 0.20 <sup>D</sup>
8	0	11.98 $\pm$ 0.21 <sup>A</sup>	2.85 $\pm$ 0.15 <sup>A</sup>
	5	10.80 $\pm$ 0.29 <sup>B</sup>	2.65 $\pm$ 0.13 <sup>AB</sup>
	10	9.43 $\pm$ 0.40 <sup>C</sup>	2.26 $\pm$ 0.1 <sup>BC</sup>
	20	9.56 $\pm$ 0.39 <sup>C</sup>	2.28 $\pm$ 0.32 <sup>BC</sup>
	30	9.20 $\pm$ 0.20 <sup>C</sup>	1.98 $\pm$ 0.28 <sup>C</sup>
	40	9.55 $\pm$ 0.18 <sup>C</sup>	2.07 $\pm$ 0.17 <sup>C</sup>
	50	9.29 $\pm$ 0.38 <sup>C</sup>	1.95 $\pm$ 0.20 <sup>C</sup>
12	0	13.22 $\pm$ 0.11 <sup>A</sup>	3.25 $\pm$ 0.16 <sup>A</sup>
	5	12.16 $\pm$ 0.17 <sup>B</sup>	3.19 $\pm$ 0.25 <sup>A</sup>
	10	11.00 $\pm$ 0.16 <sup>C</sup>	2.78 $\pm$ 0.13 <sup>B</sup>
	20	10.95 $\pm$ 0.30 <sup>C</sup>	2.76 $\pm$ 0.18 <sup>B</sup>
	30	10.58 $\pm$ 0.17 <sup>C</sup>	2.47 $\pm$ 0.21 <sup>BC</sup>
	40	10.91 $\pm$ 0.15 <sup>C</sup>	2.66 $\pm$ 0.13 <sup>BC</sup>
	50	10.73 $\pm$ 0.43 <sup>C</sup>	2.29 $\pm$ 0.30 <sup>C</sup>
24	0	14.98 $\pm$ 0.11 <sup>A</sup>	3.83 $\pm$ 0.22 <sup>A</sup>
	5	14.33 $\pm$ 0.09 <sup>B</sup>	3.79 $\pm$ 0.13 <sup>A</sup>
	10	13.53 $\pm$ 0.10 <sup>D</sup>	3.54 $\pm$ 0.13 <sup>AB</sup>
	20	13.48 $\pm$ 0.17 <sup>D</sup>	3.34 $\pm$ 0.18 <sup>BC</sup>
	30	13.56 $\pm$ 0.09 <sup>D</sup>	3.16 $\pm$ 0.15 <sup>BC</sup>
	40	13.65 $\pm$ 0.20 <sup>CD</sup>	3.54 $\pm$ 0.21 <sup>AB</sup>
	50	13.98 $\pm$ 0.43 <sup>BC</sup>	2.96 $\pm$ 0.39 <sup>C</sup>

\* Different letters within a column and per time treatment represent a significant difference as per the Tukey test ( $\alpha = 0.05$ ).

This trend was continued throughout the duration of the test, with a reduction in mean differences of moisture absorbed as the samples approached 24 hrs of exposure. These results indicated that advantages for resistance to moisture adsorption are short-lived due to the lack of a plateau over the course of 24 hrs. However, in-service use of most wood products typically experience conditions above 90% relative humidity for periods of less than 24 hours. In terms of long period of exposure, true wood-polymer composites have an advantage over a pyrolysis oil treatment due to open hydroxyl groups found within wood pyrolysis oil. The pyrolysis oil shares a similar molecular structure with lignin; however it remains highly reactive when placed within the cell lumen structure due to the lack of polymerization.



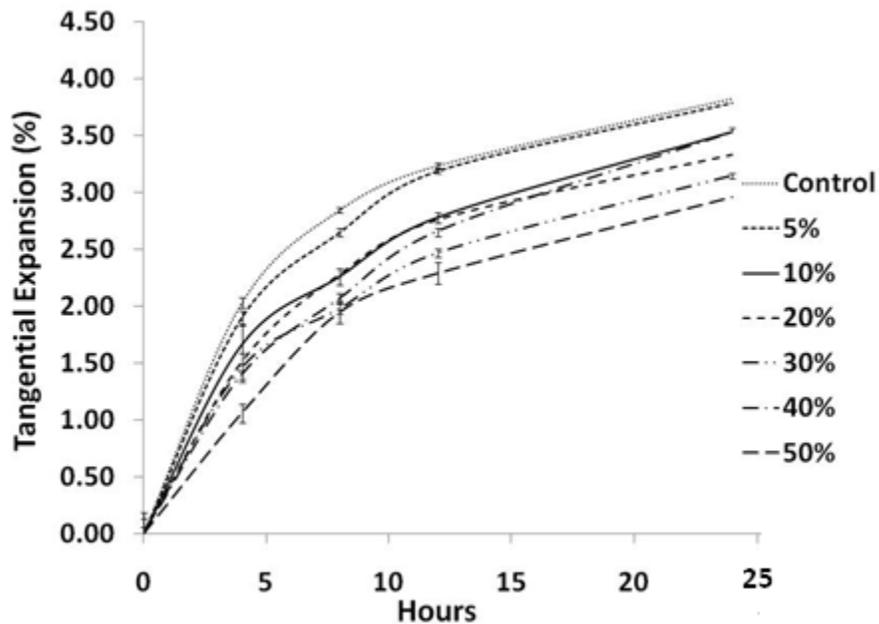
**Fig. 2.** Response of wood moisture content over time for 0:100, 5:95, 10:90, 20:80, 30:70, 40:60, and 50:50 bio-oil to methanol ratio treatments

Schneider and colleagues (1991) observed a similar trend, with moisture uptake continuing throughout the experiment. Schneider *et al.* (1991) utilized a vinyl monomer penetrant that was polymerized after its impregnation to form a NBNL polymer. As discussed earlier, a NBNL treatment has limited moisture resistant attributes, much like pyrolysis oil due to the lack of bonding between the cell wall interface and the polymeric material.

The increased tangential expansion of the treated wood demonstrated that significant reduction required a penetrant concentration of at least 10%, whereas 5% was sufficient when considering only moisture sorption. Figure 3 shows continued expansion during the 24 hr period of the test, and the rate of expansion could be explained by the rate of moisture sorption (Fig. 2).

After 4 hours, the tangential swelling continued to increase, but at a lower rate, and this was attributable to the decreased rate of moisture adsorption after 4 hours, as shown in Fig. 2. This change in slope may be an indication of the saturation of the monolayer within the cell wall.

According to the BET theory, the monolayer of moisture is bound tightly to the hydroxyl groups of wood substrate (Hartley *et al.* 1992). Thus the attraction of water molecules to the cellulose chains in wood is higher before monolayer saturation and after saturation the rate of adsorption decreases. The moisture at which the monolayer is formed is commonly 4 to 5%, and thus adsorption rates above 5% moisture should lower (Simpson 1980). This is in agreement with Fig. 2 and 3, in which the rate of adsorption in most cases above 5% moisture content.



**Fig. 3.** The response of wood expansion in the tangential direction over time for 0:100, 5:95, 10:90, 20:80, 30:70, 40:60, and 50:50 bio-oil to methanol ratio treatments

While the rate of moisture adsorption decreases above 5% moisture content for the samples in this study, there was still a lack of plateau for both moisture adsorption and consequent swelling. Overall, a loading above 20% provided optimal resistance to moisture adsorption and consequent swelling, while loadings higher than 20% provided negligible improvement. The lack of a plateau within a 24-hour period was attributable to the lack of complete polymerization within the cell wall. Scheinder *et al.* (1991) observed a plateau within a shorter time period due to polymerization of the impregnated polymer, which increased the resistance to swelling due to polymer reinforcement within the lumen of the tracheids. Conversely, pyrolysis oil remains free within the cell lumen and significant polymerization did not appear to occur in these samples based on moisture adsorption and swelling properties.

In order to compare the effectiveness of the pyrolysis oil penetrant between a vapor and liquid water environment, water submergence tests at room temperature were conducted similar to those described in Rowell and Ellis (1978) and Scheinder *et al.* (1991). As illustrated in Figs. 4 and 5, there was a negative linear relationship between increasing bio-oil concentration and water absorption ( $R^2 = 0.91$ ,  $N = 35$ ,  $df = 1,34$ ,  $F = 337.67$ ,  $p = <0.001$ ) and tangential expansion ( $R^2 = 0.71$ ,  $N = 35$ ,  $df = 1,34$ ,  $F = 40.1$ ,  $p = <0.001$ ).

Pyrolysis oil concentrations of 50% provided a tangential swelling of 4.45%, similar to the vinyl monomer swelling of 4.15% from Scheinder and colleagues (1991). Using the swelling coefficients calculated from Rowell and Ellis (1978), the pyrolysis oil treatment provided linear reductions in swelling ( $R^2 = 0.683$ ,  $N = 30$ ,  $df = 1,29$ ,  $F = 63.72$ ,  $p = <0.001$ ), with a maximum reduction of 31.1% in samples treated with the highest penetrant concentration (Table 2). Once again, the lack of a bond between the pyrolysis oil and the cell wall allows the cellulose within the wood structure to bond with free

water. In vapor tests, peak effective penetrant concentration was between 10 and 20%; however, during submergence tests, the greater the concentration, the more effective the treatment.

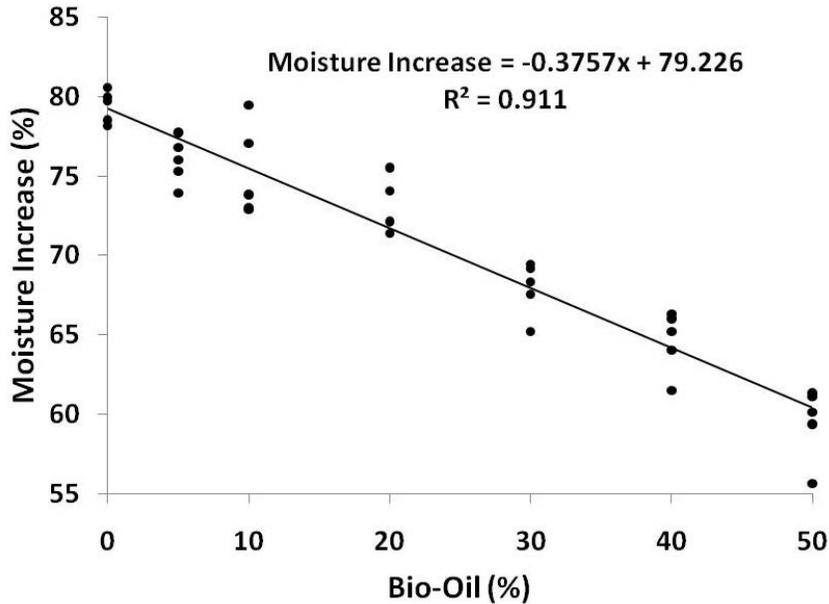


Fig. 4. The response of moisture increase (%) with bio-oil to methanol concentration with a range of 0:100 to 50:50 (bio-oil to methanol ratio)

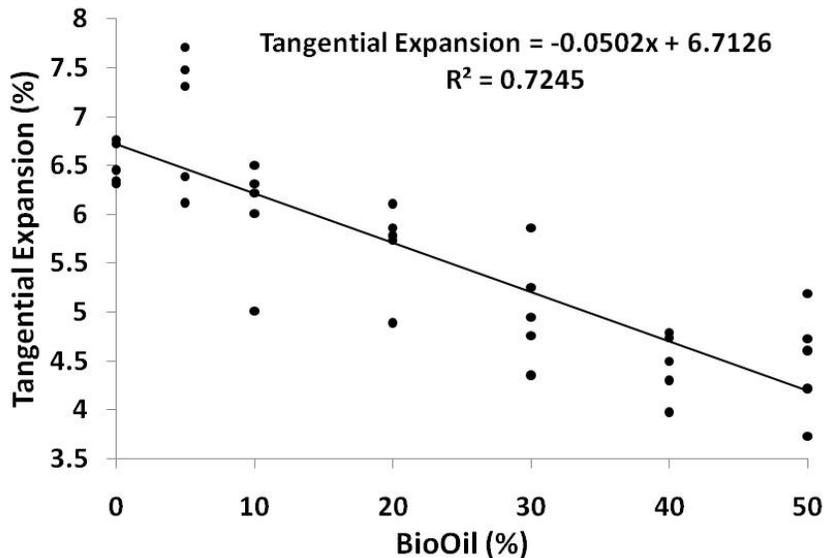
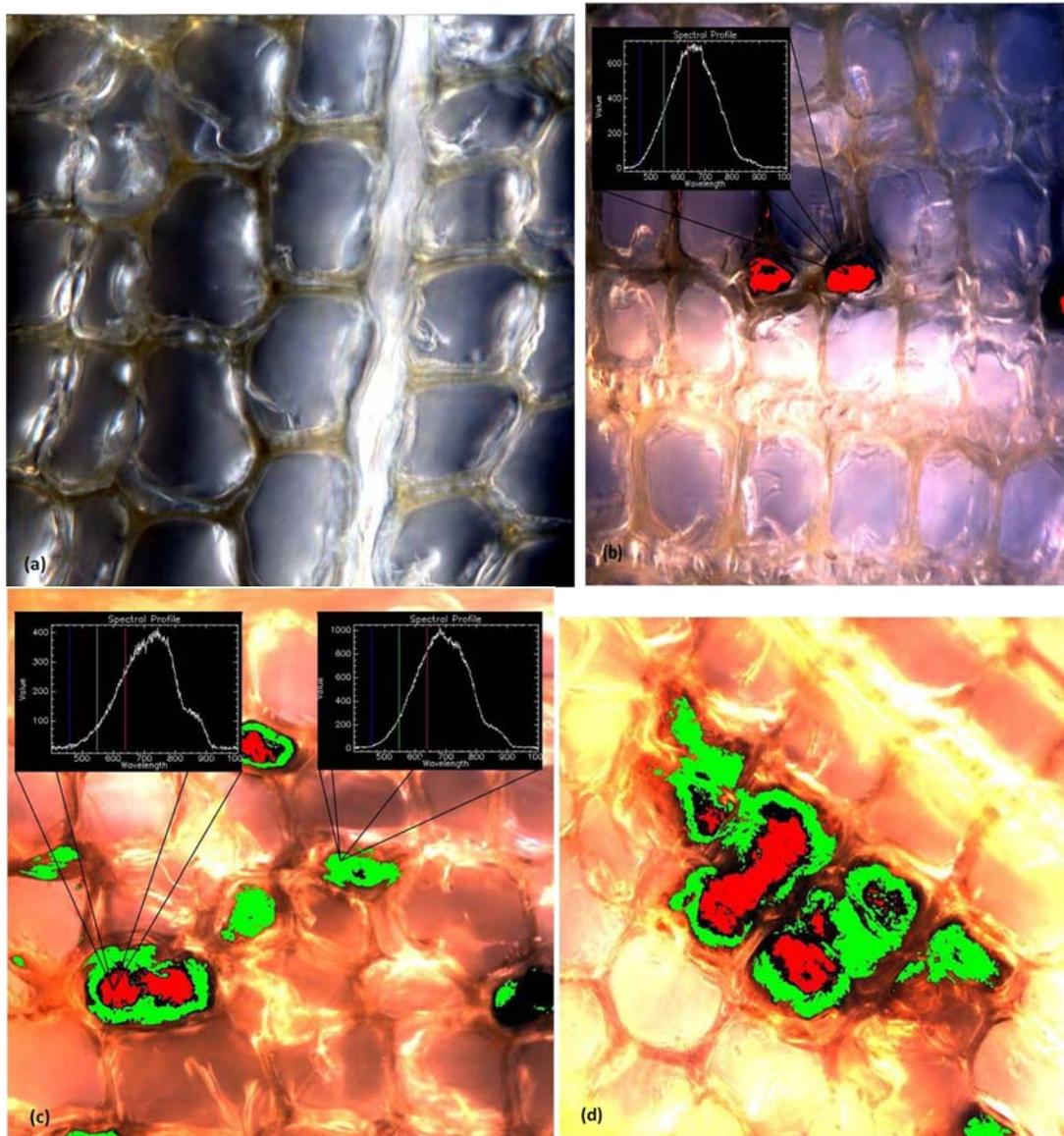


Fig. 5. The response of tangential expansion (%) with bio-oil to methanol concentration with a range of 0:100 to 50:50 (bio-oil to methanol ratio)

Due to the high degree of leachability noted in earlier research, we examined the leachability of the penetrant using a 24 hrs soak in water (Mohan et al. 2008). The moisture sorption tests were conducted prior to leaching, and would be considered a pre-leach proxy of moisture sorption. In our study, the pyrolysis oil was easily leached from the wood substrate. Gravimetric analysis of the leachate revealed a linear relationship between mass loss of pyrolysis oil during liquid water exposure ( $R^2 = 0.97$ ,  $N = 35$ ,  $df = 1$ ,  $F = 300$ ,  $p = 0.0001$ ) with an 8% loss at 50% loading. Spectrophotometric analysis of the leachate revealed a linear relationship between pyrolysis oil concentration and the amount of pyrolysis oil leached ( $R^2 = 0.99$ ,  $N = 6$ ,  $df = 1, 5$ ,  $F = 365.45$ ,  $p = <0.001$ ). Currently, research is being conducted to determine a cost-effective method for reducing this property of the penetrant. The most likely avenue is to form a true wood-polymer composite (WPC), such as a NBNL or a BNL using the high phenolic content of the pyrolysis oil as a partial substitute in a polyurethane, epoxy, or resol-type resin. In these cases, the pyrolysis oil resin is reacted within the cell structure of the wood substrate to form a bond with the cell wall and permanently fix the compound within the cell wall structure resulting in polymer bridging across the lumen resulting in bulking and resistance to swelling forces within the wood. A better way to significantly reduce moisture absorption is to inject a polymer that forms a true bond with the hydrophilic hydroxyl functional groups within the cellulose polymer, thus eliminating the ability for free water to bond (Cai et al. 2007). These reactions often impart significant swelling during cure, pushing the polymeric compound into the cellular structure and reducing or eliminating the ability of the wood to swell further under high moisture conditions. The process of impregnating wood with a hydrophobic material is not chemical modification, as is the case with acetylation. Unlike acetylation or polymer inclusion, where a true WPC is formed, the lack of bonding between the penetrant and the wood cell wall in a simple impregnation allows the product to readily leach from the wood substrate.

Using the hyperspectral microscope and mapping software, we were able to determine variation in the amount of 'free' pyrolysis oil in the wood cells (Fig. 6). Larger cell lumens were filled with the penetrant at higher concentrations. This phenomenon could be the result of increased viscosity affecting the capillary action within the lumen, or cell pore clogging, reducing the amount incorporated within smaller cells. Schneider (1994) described wood cells as acting like a chromatographic column, separating polymeric injections based on molecular weight. For this reason, the author recommended the use of monomeric materials during penetration, to aid in the even dispersion of the polymer precursors within the wood substrate. The microscopy images show a clear disparity in the distribution of the oil within the substrate when different pyrolysis oil loadings were utilized. Penetrated lumens appear congregated rather than the expected even or random distribution of filled cells. The two colors overlapped onto the images were mapped using the spectral signature of the pyrolysis oil within those regions. There is a clear distinction between the pyrolysis oil along the cell walls. This could be a result of lighter, lower molecular weight compounds entering the cell earlier and lining the cavity, followed by heavier, higher molecular weight compounds filling the lumen later. Pyrolysis oil exhibits a wide range of molecular weights, with some molecules consisting of thousands of polymeric subunits. Future research for use of this material as a moisture resistant treatment must address this problem. Pre-injection

molecular weight separation may be a necessary step in the refining of this process to provide known molecular weight fractions to determine the optimal weight for increased dispersion throughout the substrate. Future research should also consider the apparent lag time between moisture pickup and tangential swelling that occurred in this study. Longer test times may be beneficial. Finally, pyrolysis oil tends to be acidic and reactive, which could result in wood product degradation over time. The final product should thus not be utilized where acidity could degrade the wood, such as in attics, where high temperatures may persist.



**Fig. 6.** Transverse view of the penetration and distribution of Bio-oil within tracheid lumens for (a) no bio-oil/control; (b) 30:70 bio-oil to methanol; (c) 40:60 bio-oil to methanol; and (d) 50:50 bio-oil to methanol. The 2 spectra (400-1000nm) in image (c) was determined to be sensitive to the presence of pyrolysis oil and was utilized in images a-d to hyperspectrally map the location of oil within the cell lumen.

**Table 2.** Mean Tangential Swelling Coefficients (S) and Reduction in Swelling Resulting from Treatment (R) and 24hr 20°C Soak

% Pyrolysis Oil	Retention $\pm$ SD (kg/m <sup>3</sup> )	S $\pm$ SD (%)	R $\pm$ SD (%)
0	0	6.5 $\pm$ 0.002	--
5	0.7 $\pm$ 0.01	7.0 $\pm$ 0.007	7.4 $\pm$ 0.1
10	1.5 $\pm$ 0.03	6.0 $\pm$ 0.005	-7.8 $\pm$ 0.09
20	7.5 $\pm$ 0.13	5.6 $\pm$ 0.004	-12.9 $\pm$ 0.07
30	9.7 $\pm$ 0.14	5.0 $\pm$ 0.005	-22.7 $\pm$ 0.08
40	21.4 $\pm$ 0.39	4.5 $\pm$ 0.003	-31.6 $\pm$ 0.05
50	36.0 $\pm$ 0.49	4.5 $\pm$ 0.005	-31.1 $\pm$ 0.08

## CONCLUSIONS

Significant wood pyrolysis oil retention levels can be attained in southern yellow pine using low pressure methods. This process provides significant reductions in both moisture sorption and tangential expansion for short periods of time. Considering the fact that most properly installed wood products are exposed to moisture levels conducive to expansion and degradation for periods less than 24 hrs, this process provides a beneficial application of previously underutilized forest residues. As discussed, pyrolysis oil treated pine exhibits a high degree of product leaching when exposed to liquid water. Thus, future research should address the possibility of bonding the penetrant to the wood substrate in an effort to reduce product loss.

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