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# Effect of Bio-Oil and Epoxidized Linseed Oil on Physical, Mechanical, and Biological Properties of Treated Wood

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**ABSTRACT:** In this article, the effects of bio-oil and epoxidized linseed oil (ELO) on water absorption, tangential swelling, decay and insect resistance, thermo-gravimetric analysis, and mechanical properties of treated wood samples were studied. The bio-oil used in this article was by-product of ThermoWood thermal modification process. Linseed oil and hydrogen peroxide were used to prepare ELO. The results indicated that the samples treated with bio-oil had lower water absorption than that of the control group. The second treatment with ELO significantly reduced further the water absorption. The decay resistance of treated wood samples with 20% of bio-oil against brown (*Coniophora puteana*) and white rot (*Trametes versicolor*) fungi was very high. According to the insect test results, increasing bio-oil concentration from 10% to 20% significantly decreased surviving rate of *Hylotrupes bajulus*. Thermo-gravimetric analysis showed that all treated samples had higher initial deterioration temperature than that of the control group. Regarding the wood strength, the impregnated bio-oil generally reduced the mechanical properties of wood except modulus of elasticity (MOE).


**KEYWORDS:** cellulose and other wood products; degradation; mechanical properties

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## INTRODUCTION

Chromated copper arsenate was restricted as wood preservative for residential use at the end of 2003 because of its environmental concerns about the toxicity of arsenic.[1] As a consequence, new wood preservatives contain copper and organic co-biocides such as quaternary ammonium compounds (quats), azoles, borates, and/or Bis-(N-cyclohexyldiazeniumdioxy)-copper, i.e., Cu-HDO became important wood preservatives.[2–5] On the other hand, leaching of copper from the treated wood aroused as an important issue as a result of high aquatic toxicity of copper containing formulations.[6,7]

Wood protection using bioactive compounds from renewable natural products has received much attention in the recent years as a result of potential health and environmental hazards of wood preservatives containing heavy metals.[1,8–11] Research efforts on environmentally benign wood preservatives have led to several projects and publications on the products and processes that use environmental friendly technologies such as heat treatment, plant extracts, and bio-oils.

Oils obtained from biomass have a wide range of names such as pyrolysis oil, bio-oil, pyrolysis liquid, bio-crude oil, bio-fuel oil, wood liquid, wood oil, or wood distillates and become a potential an innovative wood preservative.[5,8,11,12] It was reported that bio-oils are a mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic, formic and carboxylic acid, hydroxyalhydes, hydroxyketones, sugars, and phenolics. The compounds found in bio-oils have been classified into five categories namely: (1) hydroxyaldehydes, (2) hydroxyketones,(3) sugars and dehydrosugars, (4) carboxylic acid, and (5) phenolic compounds. Phenolic compounds are derived from both coniferyl and syringyl types of lignin.[5] In contrast to coal tar, bio-oil does not contain polynuclear aromatic hydrocarbons (PAH), but contains many phenolic compounds, which possess antifungal properties.[12] Because of the complex structure of bio-oils, it is expected that they can

protect wood from biological degradation and a number of studies have reported their efficiency.[1,5,13–18]

Pyrolysis liquids from sugi and acacia wood were tested against brown rot fungi and termites. The results revealed that pyrolysis liquids increased decay resistance but did not improve termite resistance. According to the authors, the decay resistance of the studied bio-oils is because of the presence of phenolic compounds.[16]

Pine wood was pyrolyzed at various temperatures and the obtained bio-oils were tested against decay fungi, insect, and water repellency tests. Treated samples were durable against fungi. However, it was reported that the bio-oil was leachable, and thus, its performance was worsened.[5]

Mohan et al. studied several types of bio-oils and their lignin-rich fractions from pine and oak wood and bark pyrolysis. The authors stated that phenolic compounds are most likely to be the main compounds to ensure fungal inhibition.[9] It has been reported that bio-oils are leachable, and the prevention of leachability is of critically important to increase the durability of wood.[1,5,9]

The objectives of this article were to determine the hydrophobic, mechanical properties, decay and insect resistance of wood treated with bio-oil, which was obtained as by-product of ThermoWood thermal modification process. Another task was to find a method to decrease the leachability of the studied bio-oil. The synergic effect of mixing bio-oil and epoxidized linseed oil (ELO) was the focus of this article.

## EXPERIMENTAL

### Bio-Oil

The bio-oil used in this article was obtained from Novawood Company in Turkey. The used bio-oil is a by-product from ThermoWood thermal modification according to a methodology developed by VTT in Finland. ThermoWood production process is divided into three stages. At the first stage, a combination of heat and steam is used to increase the temperature of wood up to 100°C. At the second stage, heat treatment process starts and the temperature in the facility is increased to 212 ± 3°C. At the last stage, the wood passes through a cooling process and is harmonized to the ambient temperature. Bio-oil is formed by rapid and simultaneous depolymerization of cell wall components of wood during the process of thermal modification. The obtained bio-oil was blackish, very dense paste, nonsoluble in water.

### Epoxidized Linseed Oil

Linseed oil is obtained from seeds of the flax plant *Linum usitatissimum*. The oil content of flax seeds is 33–47%. The fatty acid composition of linseed oils is dominated by C18 fatty acids. The most common fatty acids in linseed oil are saturated acid (lauric, myristic, palmitic, and stearic acids) and 18-carbon polyunsaturated acids (oleic, linoliec, linolenic acids). Linseed oil is very rich in linolenic acid content (48–60%).[19] Epoxidation process of linseed oil is described in details by Panov et al. where linseed oil and hydrogen peroxide were used to prepare epoxidized linseed oil (ELO) (Figure 1).[20] Acetic acid was used as catalyst to open the epoxy rings. A previous study referred

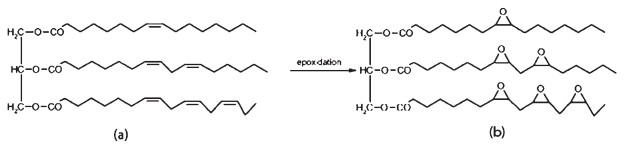


**Figure 1.** Epoxidation process of linseed oil.

that bio-oils illustrated a leachable behavior in wood but this can probably be prevented by polymerization of its compounds and/or by co-impregnation that can lead to synergistically enhanced activity.[5] Therefore, in this article, ELO was employed as potential hardener expected to decrease the leaching of the studied bio-oil and increase the hydrophobicity of wood.

### Wood Treatment Process

Scots pine sapwood (*Pinus sylvestris L.*) specimens were treated with bio-oil obtained as described above. Two treatment schedules, full and empty cell treatments, were used for bio-oil and ELO impregnation. Primary, a full cell process was applied to treat the specimens with 10% and 20% of bio-oil diluted with ethanol. As a second step impregnation, an empty cell process with ELO was applied for fixation of the bio-oil into the wood cell wall. The full cell impregnation procedure consisted of 10 min vacuum (65%) and 20 min pressure (10 bars), whereas the empty cell procedure consisted of 20 min prepressure (1.25 bars). After the period of prepressure, ELO was applied by 50 min pressure (2.5 bars) and 5 min final vacuum. After every treatment, the specimens were removed from the autoclave and weighed to determine the retention of bio-oil.

After the full cell treatment process, samples treated with bio-oil were dried at 65°C temperature for 24 h. The specimens treated with ELO were polymerized by using acetic acid in desiccator at 100 ± 2°C temperature for 3 h. Photographs of treated samples are shown in Figure 2.

### Leaching, Water Absorption and Tangential Swelling Test

Leaching test was performed according to the American Wood Preservers' Association (AWPA) E 11 standard method.[21] Treated wood specimens (15 × 25 × 50 mm) were submerged in deionized water. The water was replaced after specific time as follows: 6 h, 1, 2 days, and every 2 days to a total of 14 days. The collected water was used for a fungal inhibition test.

For Water Absorption (WA) and Tangential Swelling (TST) tests, wafers measuring 6.4 × 25 × 50 mm were prepared from Scots pine sapwood according to AWPA E4.[22] The samples were conditioned to 12% moisture content before testing. Treated and untreated samples were placed into beakers filled with deionized water. The water was replaced with fresh one after 10, 20, 30, 40, 50, 60 min and 2, 3, 4, 24, and 48 h. Mass and dimensions of the samples were recorded. Experiments were carried out at room temperature. WA and TST were calculated according to eqs. (1) and (2) after each water replacement:

$$WA = [(W2\text{-}W1)/W1]\times 100 \quad (1)$$

$$TST = [(T2\text{-}T1)/T1]\times 100 \quad (2)$$

where W1 and W2 are the mass of the wood specimens before and after test;

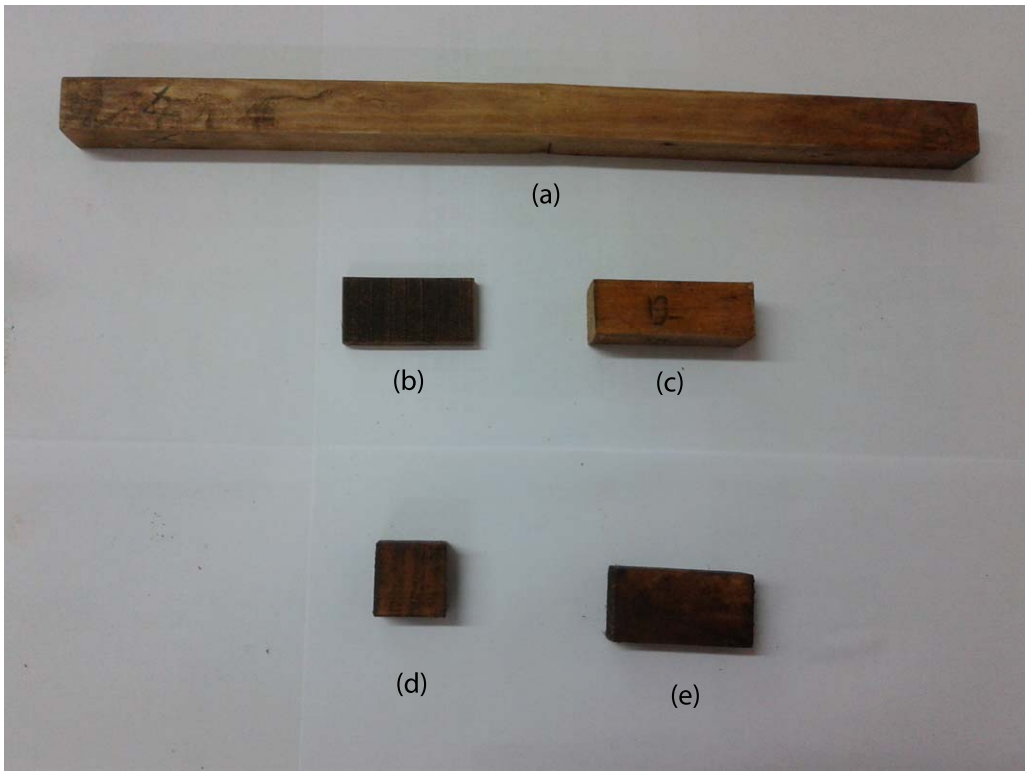


**Figure 2.** Photographs of treated samples (a) MOE and MOR sample, (b) WA and TST sample, (c) CSPG sample, (d) insect test sample, (e) decay test sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

T2 is the tangential dimension at any given time during water soaked condition;

T1 is the initial tangential dimensions of the specimen.

**Decay Test**

Decay resistance of the treated wood was tested according to the European Standard EN 113.[23] Prior to the decay test, Scots pine samples (15 × 25 × 50 mm along the grain) were leached in water according to AWPA E11 to determine the leaching effects that would occur in service.[21]

Kolle flasks containing 3% malt agar extract culture medium were inoculated with the brown rot fungus *Coniophora puteana* BAM Ebw. 15 and the white rot fungus *Trametes versicolor* CTB 863A. The treated and untreated (control) wood samples were subjected to fungal attack for 16 weeks in a climate room (22 ± 1°C and 70 ± 5% RH). At the end of the exposure time adhering mycelia were removed from the specimens, and after weighing, the specimens were oven-dried at 103 ±2 °C and reweighed. The mass loss caused by the test fungi was calculated.

**Fungal Inhibition Test of Leachates**

About 250 mL of medium (4 g agar and 5 g malt) was prepared from the collected leachates after 6 h, 1 day, and 1 week during the leaching test. Control medium (4 g agar and 5 g malt) was also prepared from distilled water as control. The test fungi were inoculated for an inhibition test. The plates were exposed at 20 ± 1°C and 65 ± 5% RH, and the growth of mycelia was monitored for 3 weeks.

**Insect Test**

Insect test was carried out according to EN 47 (2005) standard method to study the efficacy of the bio-oil and ELO against larvae of *Hylotrupes bajulus*.[24] Sample with dimensions of 15 × 25 × 25 mm along the grain were conditioned at 20 ± 2°C and 65 ± 5% RH prior to the test. Three openings, approximately 3 mm deep, were drilled in a diagonal pattern on the upper longitudinal face of each test sample. A newly hatched larva of *H. bajulus* was carefully inserted head first in each opening.

For the untreated samples, six openings in two diagonal rows were drilled and a newly hatched larva was inserted in each opening. After exposure to the larvae, the test specimens were placed on a filter paper dish in jars and stored in a controlled chamber at 20 ± 2°C and 65 ± 5% RH for 4 weeks.

After the exposure, each sample was examined by X-rays to check for dead larvae or presence of frass, which is a sign of an initial larval activity. The state of larvae (dead, living, not recovered) was recorded for all test samples.

**Strength Tests**

Modulus of elasticity (MOE), modulus of rupture (MOR), and compression strength parallel to grain (CSPG) were determined in accordance with DIN 186 and DIN 185.[25]

**Thermo-Gravimetric Analysis**

Thermo-gravimetric analyses (TGA) were conducted with a Netzsch TG 209 F1 Iris thermo-gravimetric analyzer. This method measures the changes in weight as a function of temperature changes with a resolution of 0.1 mg in a nitrogen

**Table I.** Water Absorption (WA), Tangential Swelling Test (TST) and Retention Results of the Impregnated Bio-Oil and Oil

| | | Water absorption (%) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Treatments | Retention (kg m$^{-3}$) | 10 min | 20 min | 30 min | 40 min | 50 min | 60 min | 2 h | 3 h | 4 h | 24 h | 48 h |
| 10% bio-oil | 46.37 (2.01) | 27.75$^{ca}$ (0.98)$^{b}$ | 31.60$^{c}$ (0.31) | 33.93$^{c}$ (0.84) | 33.93$^{c}$ (0.45) | 34.55$^{c}$ (0.45) | 35.44$^{c}$ (0.23) | 36.19$^{c}$ (0.14) | 38.33$^{c}$ (0.59) | 38.94$^{c}$ (0.29) | 49.52$^{c}$ (0.12) | 59.61$^{d}$ (0.09) |
| 10% bio-oil + ELO | 44.33 (2.02) | 1.91$^{a}$ (0.01) | 3.05$^{a}$ (0.12) | 4.00$^{a}$ (0.00) | 4.00$^{a}$ (0.37) | 4.61$^{a}$ (0.13) | 5.23$^{a}$ (0.01) | 6.69$^{a}$ (0.37) | 8.28$^{a}$ (0.64) | 9.15$^{a}$ (0.64) | 18.03$^{a}$ (0.90) | 20.99$^{a}$ (0.67) |
| 20% bio-oil | 99.05 (2.74) | 14.53$^{b}$ (2.20) | 19.15$^{b}$ (2.19) | 22.46$^{b}$ (2.32) | 22.77$^{b}$ (1.78) | 24.23$^{b}$ (1.67) | 24.74$^{b}$ (1.67) | 25.76$^{b}$ (1.57) | 27.21$^{b}$ (1.60) | 27.34$^{b}$ (1.84) | 35.81$^{b}$ (1.44) | 43.03$^{c}$ (1.51) |
| 20% bio-oil + ELO | 100.79 (0.83) | 1.93$^{a}$ (0.20) | 2.90$^{a}$ (0..20) | 4.03$^{a}$ (0.41) | 4.51$^{a}$ (0.40) | 4.92$^{a}$ (0.28) | 5.40$^{a}$ (0.50) | 7.42$^{a}$ (0.08) | 8.63$^{a}$ (0.24) | 9.43$^{a}$ (0.01) | 18.14$^{a}$ (0.13) | 21.29$^{a}$ (0.24) |
| Only ELO | 202.50 (24.04) | 1.59$^{a}$ (0.47) | 2.45$^{a}$ (0.57) | 3.55$^{a}$ (0.87) | 4.22$^{a}$ (0.81) | 5.04$^{a}$ (0.89) | 5.76$^{a}$ (0.76) | 8.35$^{a}$ (0.48) | 9.93$^{a}$ (0.53) | 10.99$^{a}$ (0.49) | 20.39$^{a}$ (0.74) | 26.53$^{b}$ (1.40) |
| Control | - | 56.77$^{d}$ (2.38) | 57.89$^{d}$ (2.54) | 59.79$^{d}$ (2.29) | 59.97$^{d}$ (2.00) | 60.95$^{d}$ (2.19) | 60.59$^{d}$ (2.13) | 60.56$^{d}$ (1.90) | 61.39$^{d}$ (2.00) | 62.33$^{d}$ (2.00) | 68.71$^{d}$ (1.89) | 75.05$^{e}$ (2.26) |
| Tangential swelling (%) | | | | | | | | | | | | |
| 10% bio-oil | 46.37 (2.01) | 5.37$^{ca}$ (0.05)$^{b}$ | 5.57$^{c}$ (0.05) | 5.65$^{c}$ (0.05) | 5.68$^{b}$ (0.08) | 5.76$^{bc}$ (0.13) | 5.75$^{b}$ (0.11) | 5.83$^{b}$ (0.11) | 5.92$^{c}$ (0.17) | 5.99$^{c}$ (0.19) | 6.10$^{bc}$ (0.10) | 6.10$^{a}$ (0.10) |
| 10% bio-oil + ELO | 44.33 (2.02) | 0.42$^{a}$ (0.14) | 0.85$^{a}$ (0.19) | 1.04$^{a}$ (0.04) | 1.38$^{a}$ (0.13) | 1.50$^{a}$ (0.07) | 2.07$^{a}$ (0.09) | 2.60$^{a}$ (0.19) | 3.10$^{a}$ (0.18) | 3.52$^{a}$ (0.29) | 5.32$^{ab}$ (0.15) | 5.48$^{a}$ (0.13) |
| 20% bio-oil | 99.05 (2.74) | 3.77$^{b}$ (0.37) | 4.75$^{b}$ (0.20) | 5.27$^{b}$ (0.16) | 5.53$^{b}$ (0.03) | 5.70$^{b}$ (0.02) | 5.76$^{b}$ (0.11) | 5.82$^{b}$ (0.11) | 5.88$^{c}$ (0.14) | 5.94$^{c}$ (0.10) | 6.06$^{bc}$ (0.06) | 6.12$^{a}$ (0.11) |
| 20% bio-oil + ELO | 100.79 (0.83) | 0.25$^{a}$ (0.10) | 0.58$^{a}$ (0.43) | 1.00$^{a}$ (0.35) | 1.38$^{a}$ (0.43) | 1.66$^{a}$ (0.51) | 1.84$^{a}$ (0.27) | 2.65$^{a}$ (0.40) | 3.27$^{ab}$ (0.42) | 3.60$^{a}$ (0.30) | 5.33$^{ab}$ (0.04) | 5.39$^{a}$ (0.01) |
| Only ELO | 202.50 (24.04) | 0.37$^{a}$ (0.08) | 0.75$^{a}$ (0.28) | 1.00$^{a}$ (0.27) | 1.31$^{a}$ (0.22) | 1.67$^{a}$ (0.19) | 2.02$^{a}$ (0.15) | 2.92$^{a}$ (0.10) | 3.61$^{b}$ (0.03) | 3.99$^{b}$ (0.10) | 4.77$^{a}$ (1.00) | 5.37$^{a}$ (0.08) |
| Control | - | 5.92$^{d}$ (0.19) | 5.99$^{d}$ (0.21) | 6.04$^{d}$ (0.22) | 6.08$^{c}$ (0.24) | 6.10$^{c}$ (0.22) | 6.13$^{c}$ (0.23) | 6.17$^{b}$ (0.23) | 6.18$^{c}$ (0.21) | 6.15$^{c}$ (0.21) | 6.20$^{c}$ (0.19) | 6.04$^{a}$ (0.67) |

[a] Similar letter indicates no statistical significance.

[b] Numbers in parenthesis are standard deviation.



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atmosphere. About 10 mg of wood samples were analyzed and heated from 20°C to 600°C at a rate of 20°C/min in a platinum sample pan.

## RESULTS AND DISCUSSION

### Chemical Structure of Bio-Oil

Bio-oils are de-polymerization products of the wood cell wall components. Hemicellulose is thermally the most sensitive cell wall component.[26,27] During the thermal degradation, acetic acid, which causes acid-catalyzed degradation of the polysaccharides, is formed from acetylated hemicelluloses by hydrolysis. It is reported that cellulose degradation occurs at a higher temperature than that of hemicelluloses. Levoglucosan has been identified as the primary breakdown products from cellulose during the thermal treatment but other anhydroglucoses, furan, and furan derivates are also produced. Lignin is the most thermally stable component of cell wall. Through heat treatment, bonds between the phenylpropane units are partly broken. The lignin degradation by heat treatment yields various phenolic breakdown products.[28] Depolymerized wood components are almost entirely composed of carbon, hydrogen, and oxygen.[9] Bio-oil has complex chemical structures and its compounds are reported as follows: 20–30% pyrolytic lignin, 10–20% carboxylic acids (acetic, formic, propionic, and glycolic as the major carboxylic acids, with butyric, pentanoic, and hexanoic present in small amounts), 14–25% aldehydes (primarily glycoaldehyde, glyoxal, hydroxypropanol, methyl glyoxal, and smaller amounts of formaldehyde, acetaldehyde, 2-furaldehyde, and syringaldehyde), 5–15% sugars (levoglucosan, fructose, cellobiosan, and glucose, along with lower concentrations of other compounds including various oligosaccharides, anhydroglucofuranose), 4–10% ketones (primarily hydroxypropane, cyclopentanone, cyclopentene, furanone, hydroxymethylpyrone, and others at lower concentrations including butyrolactone, acetyloxyprapanone), 2–10% alcohols (acetol, methanol, ethylene glycol), and 2–8% solids content.[9,28]

### Water Absorption and Tangential Swelling

The retention, WA, and TST results of the treated wood samples are listed in Table I.

WA values of the control groups showed an increase from 56% to 75% after 48 h of exposure in water. The studied bio-oil and ELO showed significantly lower WA results than the untreated (control) group. The results clearly show that the second treatment with ELO significantly reduced the WA of the samples treated with bio-oil. The possible explanation could be the fatty acids in the linseed oil. Linoleic acid, one of the main acid in the linseed oil has double C=C. When the bond is epoxidized, it becomes very reactive to hydroxyl groups of wood and thus, the absorption is decreased.

Tangential swelling of control and bio-oil treated samples showed highest values but the second treatment with ELO significantly reduced the initial tangential swelling. ELO treatment showed higher ASE results initially and decreased with the increasing soaking time in water.

### Decay Test

Weight losses and moisture content of wood treated with bio-oil and ELO against the test brown and white rot fungi are shown in Table II.

All treated samples had significantly lower mass loss than the untreated samples. The mass loss of the control (untreated) samples was higher than 20% (15% for the white rot fungus), thus confirming the validity of the test. Decay resistance of treated wood samples with 20% of bio-oil against brown and white rot fungi was very effective (less than 3% mass loss). The second impregnation with ELO slightly increased the mass loss caused by decay fungi; however, the ELO treatment significantly decreased the water uptake confirmed by WA test.

It might be concluded from the decay test results that the increased decay resistance of wood treated with bio-oil against the brown and white fungi tested can be attributed to the presence of phenolic compounds. It is reported that phenolic compounds are the main active compounds for any antimicrobial activity.[9] Antioxidant activity of phenolic products in bio-oils is based on the behavior of substituted phenolic antioxidants. Degradation mechanism of fungal attack to wood can be because of oxidative attack and breakdown of lignin by hydroxyl

**Table II.** Weight Losses and Moisture Content of the Specimens after Decay Test

| | Weight losses (%) | | | | Moisture content (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | Test | | Control | | Test | | Control | |
| Treatment | Average | St.D. | Average | St.D. | Average | St.D. | Average | St.D. |
| *Trametes versicolor* | | | | | | | | |
| 10% bio-oil | 2.23 | 0.40 | 16.03 | 2.73 | 26.91 | 1.43 | 50.40 | 4.49 |
| 10% bio-oil + ELO | 6.10 | 1.00 | 14.59 | 1.76 | 27.40 | 0.70 | 51.10 | 3.21 |
| 20% bio-oil | 1.35 | 0.38 | 18.13 | 4.71 | 26.14 | 0.35 | 57.14 | 9.44 |
| 20% bio-oil + ELO | 3.41 | 0.31 | 15.58 | 1.39 | 25.49 | 0.32 | 50.87 | 2.87 |
| *Coniophora puteana* | | | | | | | | |
| 10% bio-oil | 1.53 | 0.79 | 27.19 | 5.52 | 30.58 | 4.67 | 78.64 | 13.74 |
| 10% bio-oil + ELO | 2.43 | 1.82 | 30.17 | 5.70 | 27.96 | 3.07 | 91.60 | 19.99 |
| 20% bio-oil | 1.44 | 0.74 | 29.61 | 5.84 | 25.80 | 1.16 | 84.00 | 12.77 |
| 20% bio-oil + ELO | 4.90 | 3.10 | 22.46 | 1.23 | 25.80 | 0.80 | 70.83 | 7.28 |

**Table III.** Fungal Growth Rate

| | After 1 week | | | | | |
|---|---|---|---|---|---|---|
| | 6 h leachate | | 1 day leachate | | 1 week leachate | |
| Treatment | *T.V.* | *C.P.* | *T.V.* | *C.P.* | *T.V.* | *C.P.* |
| 20% bio-oil + ELO | 5.50 mm | - | 4.50 mm | - | 5.00 mm | 4.50 mm |
| 20% bio-oil | 6.00 mm | 7.10 mm | 7.50 mm | 6.90 mm | 7.00 mm | 6.10 mm |
| 10% bio-oil + ELO | 7.00 mm | - | 5.80 mm | - | 8.75 mm | 9.00 mm |
| 10% bio-oil | 6.50 mm | 7.20 mm | 7.70 mm | 7.70 mm | 7.80 mm | 6.90 mm |
| Control | 7.50 mm | | | | | |
| After 2 weeks | | | | | | |
| 20% bio-oil + ELO | 7.00 mm | - | 6.40 mm | - | 5.30 mm | 6.60 mm |
| 20% bio-oil | 7.10 mm | 7.20 mm | 9.00 mm | 8.00 mm | 8.20 mm | 6.40 mm |
| 10% bio-oil + ELO | 9.00 mm | - | 9.00 mm | - | 9.00 mm | 9.00 mm |
| 10% wood tar | 9.00 mm | 7.70 mm | 9.00 mm | 9.00 mm | 9.00 mm | 9.00 mm |
| Control | 9.00 mm | | | | | |
| After 3 weeks | | | | | | |
| 20% bio-oil + ELO | 7.00 mm | - | 6.60 mm | - | 6.00 mm | 6.60 mm |
| 20% bio-oil | 6.90 mm | 7.00 mm | 9.00 mm | 8.00 mm | 8.30 mm | 6.20 mm |
| 10% bio-oil + ELO | 9.00 mm | - | 9.00 mm | - | 9.00 mm | 9.00 mm |
| 10% bio-oil | 8.00 mm | 8.50 mm | 9.00 mm | 9.00 mm | 9.00 mm | 9.00 mm |
| Control | 9.00 mm | | | | | |

radicals.[29] Thus, the phenolic compounds may act as a stoichiometric sink to react with hydroxyl radicals, thus preventing attack against the wood structure.[9]

Similar results were found by several researchers. Kartal et al. studied pyrolysis liquids from sugi and acacia wood and found decay resistance against brown-rot fungi. The authors attributed the decay resistance of wood treated with pyrolysis liquids to the phenolic compounds in oil.[16]

Anti-fungal properties of pyrolytic oil derived from softwood bark were investigated by Mourant et al.[17] It was concluded that the high phenolic content in the bio-oil had anti-fungal effect.[17]

Mazela also reported fungicidal properties of wood tar extracted by pyrolysis of wood previously treated with creosote.[30]

Pine and oak wood and barks were pyrolyzed by Mohan et al.[9] Bio-oils were fractionated to obtain lignin-rich fractions that consist mainly of phenols. Results showed that lignin-rich fractions exhibited great fungal inhibition.[9]

Bio-oils obtained from pyrolysis of pistachios' shell were tested and showed fungicidial activity.[12]

Bio-oil can be considered as an alternative to creosote, which is obtained from the fractional distillation of crude coal tar produced by high temperature carbonization of bituminous coal. In contrast to creosote, bio-oil does not contain PAH but contains many phenolics which are effective against decay fungi. PAH are dangerous pollutants for the environment and humans' health as they can cause irritation.[31] In accordance with The AWPA, creosote retention of pine wood to be used in ground contact or fresh water is around 160 kg $m^{-3}$. In the case of more severe conditions and extreme decay potential, a creosote retention increases to 192 kg $m^{-3}$. On the other hand, in marine applications, the creosote retention level is 400 kg $m^{-3}$ for pine wood.[32] In this article, the retention target of the bio-oil studied was 50–100 kg $m^{-3}$ which is industrially applicable and economically viable.

Kartal et al. reported that 460 kg $m^{-3}$ average retention of the bio-oil was enough to protect against all the fungi and termites tested in their study.[8] Mohan et al. concluded that the bio-oils were considerably more effective against brown rot than the white rot with a toxic threshold values in the range of 96–192 kg $m^{-3}$ oil.[9]

### Fungal Inhibition Test of Leachates

The results from the fungal inhibition test are shown in Table III.

According to the fungal inhibition test results of leachates, the control groups, which are prepared from distilled water, showed biggest mycelium growth as expected. Fungal growth was not observed in the solutions containing ELO for *C. puteana* except from leachates obtained after 1 week immersion. It seems that 10% and 20% of bio-oil leachates do not show any inhibition effects against brown and white rot fungi. It can be concluded from fungal inhibition test that some toxic substances are released during leaching test. However, this is a preliminary study, and further studies with analytical technique should be done.

In addition to protection of wood against destroying organisms, improving hydrophobicity of bio-oil is highly desired because biocide effectiveness could be improved by reduced moisture

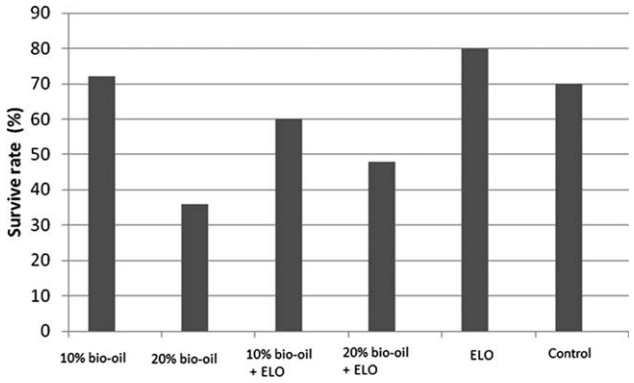


**Figure 3.** Insect test results against larvae of *H. bajulus*.

absorption of the treated wood. Previous studies revealed that bio-oils are leachable.[1,5,9] The second step impregnation with ELO was carried out to possible reduce the leaching of bio-oil.

### Insect Test

Insect test results with the larvae of *H. bajulus* are shown in Figure 3.

More than 70% of the larvae in the control samples survived after 4 weeks of exposure, i.e., the test was valid. The results show that 10% of bio-oil and only ELO treatments were not efficient against *H. bajulus* but dual treatment of bio-oil and ELO has some positive effect. Increasing bio-oil concentration from 10% to 20% significantly decreased surviving rate of *H. bajulus*. It was reported that pure bio-oils obtained from Scots pine at different temperatures of pyrolysis process were effective against *H. bajulus*.[5] However, in this article, only 10% and 20% of bio-oil were tested.

High surviving rate of ELO-treated samples against *H. bajulus* can be attributed to low retention of ELO (200 kg $m^{-3}$) and its nontoxic properties against *H. bajulus*.

### Strength Tests

MOE, MOR, and CSPG of wood samples treated with bio-oil are shown in Table IV.

The treatment with bio-oil generally reduced the mechanical properties of wood except MOE. The decrease of MOR and CSPG of treated wood might be because of bio-oil's complex chemistry and reactions with wood. Bio-oils are composed of mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic, formic and carboxylic acid, hydroxyalhydes, hydroxyketones, sugars, and phenolics.[9,19] Because of their amphoteric properties, some bio-oil components may penetrate into the cell wall and change the mechanical properties. The strength losses of wood caused by wood preservatives are related directly to its chemistry and severity of its fixation/precipitation reaction with wood.[9,33]

### Thermo-Gravimetric Analysis

TGA results of the treated wood are shown in Table V.

According to TGA results, 10% of bio-oil treated wood showed highest initial and deterioration temperatures than those of other treated samples, whereas control group exhibited the lowest initial and deterioration temperatures. Second impregnation of bio-oil (20%) with ELO increased initial temperature but the deterioration temperature slightly decreased. It can be concluded that treated samples have higher deterioration temperatures than the temperature of the control samples.

## CONCLUSIONS

Bio-oil from Thermowood thermal modification process was evaluated in this article. WA, tangential swelling, decay resistance against brown rot and white rot, insect test, TGA and mechanical properties of treated wood samples were studied. In order to decrease the leachability of bio-oil, ELO was impregnated additionally.

**Table IV.** Mechanical Test Results of Bio-Oil

| Treatment | MOR (N $mm^{-2}$) | MOE (N $mm^{-2}$) | CSPG (N $mm^{-2}$) |
|---|---|---|---|
| 10% bio-oil | 79.61 (5.32)[ba] | 13087.56 (1611.85)[aa] | 47.46 (2.76)[a] |
| 20% bio-oil | 74.80 (12.91)[a] | 12928.52 (1684.34)[a] | 54.64 (2.57)[b] |
| Control | 91.72 (14.78)[b] | 12963.87 (1691.49)[a] | 56.67 (6)[bc] |

[a] Similar letter indicates no statistical significance.
[b] Numbers in parenthesis are standard deviation.

**Table V.** Thermogravimetric Analyses (TGA) Results of Treated Wood

| Treatment | Initial temp. (°C) | Deterioration temp. (°C) | TG/ % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 20% | 30% | 40% | 50% | 60% | 70% | 80% | 90% |
| 20% bio-oil | 304.1 | 369.6 | 506.9 | 386.3 | 369.7 | 357.3 | 339.9 | 316.7 | 285.6 | 248.6 |
| 20% bio-oil + ELO | 320.2 | 368.1 | 465.8 | 415.8 | 388.2 | 373.4 | 362.7 | 349.1 | 327.6 | 289.3 |
| 10% bio-oil | 327.9 | 370.7 | 454.6 | 415.3 | 391.7 | 376.7 | 365.9 | 352.9 | 331.3 | 292.3 |
| Only ELO | 322.8 | 363.2 | 541.1 | 433.8 | 381.5 | 366.8 | 357.5 | 345.0 | 326.5 | 296.1 |
| Control | 303.4 | 345.4 | 498.6 | 426.3 | 362.5 | 349.8 | 340.1 | 327.1 | 309.0 | 278.3 |

According to the results, the hydrophobic characteristic of samples treated with bio-oil was higher than that of control (untreated) samples. Second step impregnation with ELO increased the hydrophobicity. Decay resistance of treated wood samples with 20% of bio-oil against brown (*C. puteana*) and white rot (*T. versicolor*) fungi was remarkable (less than 3% mass loss). Increasing bio-oil concentration from 10% to 20% significantly decreased the surviving rate of *H. bajulus*. Mechanical test results show that impregnation with bio-oil generally decreases the mechanical properties of wood except MOE. TGA revealed that treated samples have higher deterioration temperatures than that of control samples.

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