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Efficacy of tar oil recovered during slow pyrolysis of macadamia nut shells

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ABSTRACT

Decay and termite resistance of wood treated with tar oil obtained from a commercial pyrolysis process of macadamia nut shells was evaluated. Vacuum-treated pinewood specimens were subjected to two brown- and two white-rot fungi based on the soil-block test method specified by the American Wood Protection Association after a 10-day-leaching process. Treated specimens were also subjected to the subterranean termite attack according to Japanese Industrial Standards (JIS) for 3 weeks under laboratory conditions. In the study, growth inhibition of selected fungi with the tar oil was also tested in vitro. Treated wood specimens at a retention level of 460 kg m^{-3} showed good protection against all the fungi tested. Mass losses in leached specimens were less than those observed in unleached specimens. Similar results were seen when the specimens were subjected to termite attack. Inhibition tests showed that higher concentrations of the tar oil are critical for inhibition of the brown-rot fungi compared to the concentrations required to impede the white-rot and sap-staining fungi tested.

1. Introduction

As natural products, wood extractives and essential oils might be possible approaches for developing new wood preservatives due to their fungitoxic and insecticidal properties (Hon and Shiraishi, 1991; Schultz and Nicholas, 2002; Burt, 2004; Smith et al., 2005). Renewable and alternative sources for wood protection have received much attention in recent years since there is an increasing incentive to develop environmentally benign wood preservatives due to the restrictions of certain wood preservatives containing heavy metals, and environmental concerns about broad-spectrum biocides (Voda et al., 2003; Burt, 2004; Holley and Patel, 2005; Park and Shin, 2005; Smith et al., 2005; Mater et al., 2006; Sim et al., 2006; Yi et al., 2006). Considerable attention has also been focused on producing fuels, carbonized materials, and a wide range of chemicals from biomass by pyrolysis or carbonization processes (Chen et al., 2001). While forestry and forest industry residues, such as waste wood, sawdust, tree branches, bark, and needles, are major components of biomass, agricultural wastes, such as the shells of nuts, are also an important biomass constituent. Liquids from the pyrolysis of biomass, called pyrolysis oil, bio-oil, bio-crude, bio-fuel oil, tar oil, or wood vinegar, are generally dark brown and viscous liquids. Depending on the process conditions and the type of biomass, such liquids may contain very complex and diverse chemical components such as fermentable sugars, furan compounds, phenolic compounds, organic acids, tar and oil, gases, and alcohols (Fengel and Wegener, 1984; Kartal et al., 2004). Heo et al. (2010) have stated that fast pyrolysis refers to a process at temperatures of about 500 °C with very high heating rates maximizing the conversion of biomass into mostly liquid products. However, in slow pyrolysis, the main product after the process is char along with pyrolysis oils, which are substantially free of polynuclear aromatic hydrocarbons but rich in phenolics, which may have potential as wood preservatives (Mohan et al., 2008).

Because of the complex structure of pyrolysis liquids, they might be expected to protect the wood from biological degradation (Mansoor and Ali, 1992; Lutomski, 1997; Perez and Cortez, 1997; Suzuki et al., 1997; Meier et al., 2001; Kartal et al., 2004; Mourant et al., 2005, 2007). Previous studies by Sameshima et al. (2002) and Yatagai et al. (2002) correlated the termiticidal activity of wood vinegars with phenolic and acetic acid content from charcoal production. Kartal et al. (2004) found that pyrolysis liquids from sugi and acacia wood showed increased resistance against the brown-rot fungi tested; however, they showed no resistance

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against subterranean termite attack. The effectiveness of liquids from pyrolysis of solid wood and wood-based composites such as particleboard, plywood, and medium-density fiberboard (MDF) to control fungal growth in vitro was examined with consideration of the bio-active components included in the liquids (Nakai et al., 2007). Fungicidal tests showed a significant difference in fungi control between solid wood and composites, and liquids from the composites exhibited greater effectiveness against the white-rot fungus *Trametes versicolor* and the brown-rot fungus *Tyromyces palustris*. Mazela (2007) stated that wood tar extracted by pyrolysis of retired creosote-treated wood might have potential as either a preservative to protect wood or a component of preservatives. More recently, Mohan et al. (2008) studied several types of bio-oils and their lignin-rich fractions from wood and bark pyrolysis. Their results showed that the bio-oils were considerably more effective against the brown-rot fungus than the white-rot fungus tested.

In this study, wood specimens treated with tar oil from the slow pyrolysis of macadamia nut shells were examined by laboratory decay and termite-resistance tests using brown-rot and white-rot fungi and subterranean termites. Inhibitory effects in vitro of filtrates on the growth of brown-rot, white-rot, and sap-staining fungi were also evaluated.

2. Materials and methods

2.1. Tar oil

Tar oil obtained from Alterna Energy (Pty) Ltd, South Africa, was recovered during slow pyrolysis of macadamia nut shell biomass by a proprietary process called the van Aardt process. The tar oil recovered from this process is a slightly viscous and dark brown oily liquid with a specific gravity of 1.10 and 1.25. Its water content varied between 15 and 30% along with water-insoluble materials (20%). It had empyreumatic and burnt, charred, smoky odor. Its pH varied from 2.0 to 3.5. Some other properties of the tar oil are given in Table 1 (unpublished data). The tar oil also included the following specific hydrocarbons, some only in the parts-per-million range: 1,2,4 trimethylbenzene; 1,3,5 trimethylbenzene; acenaphthene; acenaphthylene; anthracene; benzene; benzo[a]anthracene; benzo[a]pyrene; benzo[ghi]perylene; benzo[k+b]fluoranthene; C10 (n-decane); C11 (n-undecane); C12 (n-dodecane); C13 (n-tridecane); C14 (n-tetradecane); C15 (n-pentadecane); C16 (n-hexadecane); C17 (n-heptadecane); C18 (n-octadecane); C19 (n-nonadecane); carbon; crysene; dibenz(ah)anthracene; ethylbenzene; fluoranthene; fluorene; indeno [123-cd]pyrene; naphthalene; phenanthrene; pyrene; toluene; and xylene. The amounts of benzo[a]anthracene and benzo[a]pyrene are below 100 ppm. As phenolics, phenol, O-Cresol, and 2,4 dimethylphenol were also identified in the tar oil (unpublished data).

2.2. Treatments

Wood specimens were prepared from sapwood portions of the Scots pine (*Pinus sylvestris* L.) tree. The blocks were free of knots and visible concentration of resins, and showed no visible evidence of infection by mold, stain, or wood-destroying fungi. All specimens were pre-weighed and conditioned at 20 °C and 65% RH (relative humidity) for 2 weeks before treatments with tar oil. Specimens were vacuum-treated (45-min vacuum at 550-mm Hg) with tar oil solutions without any dilution. Treated specimens were dried at 40 °C for 3 days and re-conditioned at 27 °C and 70% RH for two weeks.

Table 1
Some properties of the tar oil used in the study.

Solids (wt%)	<1
Viscosity (cSt @ 40 °C)	35.4
Ash (wt%)	<0.3
C (wt%)	41.0
H (wt%)	7.8
N (wt%)	<0.2
S (wt%)	<0.05
O (wt%)	52.0

2.3. Leaching

Leaching tests were conducted according to the Japanese Industrial Standard A 9201 (JIS, 1991). The leaching process involved immersing wood blocks in distilled water, stirring with a magnetic stirrer (400–500 rpm) at 27 °C for 8 h, followed by drying at 60 °C for 16 h. This cycle was repeated nine times. After each leaching cycle, water was replaced at a ratio of 10 volumes of water to 1 volume of wood.

2.4. Decay-resistance tests

Decay resistance was tested by exposing sapwood specimens (19 × 19 × 19 mm) to one of the following: white-rot fungi *Coriolus versicolor* (L.:Fr.) Quél. COV 1030 (*T. versicolor* (L.:Fr.) Pilát), *Pleurotus ostreatus* (Jacq.:Fr.) P. Kumm. PLO 9669; brown-rot fungi *Fomitopsis* (*Tyromyces) palustris* (Berkeley et Curtis) Murrill (FFPRI 0507); or *Neolentinus lepideus* (Fr.:Fr.) Redhead & Ginns LEL 8719 (*Lentinus lepideus*). A soil-block test was done for 12 weeks according to the AWPA E10-06 standard method (AWPA, 2007a,b). Ten leached and unleached specimens were tested for each fungus and group.

2.5. Termite-resistance tests

Untreated and treated specimens (20 × 20 × 10 mm) were exposed to the subterranean termites *Coptotermes formosanus* Shiraki, according to the JIS K 1571 standard method (JIS, 2004). An acrylic cylinder (80 mm in diameter, 60 mm in height), the lower end of which was sealed with a 5-mm-thick hard plaster (GC New Plastone, Dental Stone, GC Dental Industrial Corp., Tokyo, Japan) was used as a container. A test specimen was placed at the centre of the plaster bottom of the test container. A total of 150 worker termites collected from a laboratory colony of the Research Institute for Sustainable Humanosphere (RISH), Kyoto University, Japan, were introduced into each test container together with 15 termite soldiers. Five wood specimens per treatment were assayed against the termites. The assembled containers were set on damp cotton pads to supply water to the specimens and kept at 28 °C and >85% RH in darkness for three weeks. The mass losses of the specimens due to termite attack were calculated based on the differences in the initial and final oven-dry (60 °C, 3 days) weights of the specimens after cleaning off the debris from the termite attack. Five leached and unleached specimens were tested for each group.

2.6. Assessment of inhibition of fungal growth

The tar oil was also used to determine its ability to inhibit growth of various fungi by inclusion in 2%, w/v MEA (malt extract agar) dishes in vitro. The mutant strain brown-rot fungi *T. palustris* and *L. lepideus*, white-rot fungi *T. versicolor* and *P. ostreatus*, and sap-staining fungus *Ophiostoma piliferum* (Fr.:Fr.) Syd. & P. Syd. CPI 6702 (*Ceratocystis pilifera*) cultures (7 days old) were incubated on 2% MEA plates at 27 °C and were used for the preparation of inocula. Growth inhibition of the fungi used on 2% agar plates was tested by incorporating the tar oil at varying dilutions prepared with liquid growth medium (2% MEA) (1/10,000, 1/5000, 1/1000, and 1/500 v/v). The growth medium and tar oil solutions were autoclaved for 15 min at